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MEASUREMENT OF OPACITY DURING THE COAGULATION OF THE CONCENTRATED SOLS OF ZIRCONIUM AND STANNIC HYDROXIDES AND THE GELATION OF STANNIC PHOSPHATE AND ZIRCONIUM HYDROXIDE GEL-FORMING MIXTURES

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Received April 8, 1940

Since the classical researches of Powis[1] and the mathematical treatment of the process of coagulation by Smoluchowsky[2] various methods have been employed from time to time to study the phenomenon of coagulation. More extensively used of these are the methods depending upon the measurement of changes in viscosity and optical properties. Amongst the latter methods those involving the measurement of transparency, turbidity and refractive index have been commonly used. The spectroscopic method of Mukherjee and Papa Constantinou[3] and the tyndallmeter method of Ghosh[4] form some of the attempts in this direction. The refractive index method has been used extensively by Joshi and co-workers[5] during their study of the phenomenon of slow coagulation.

Krishnamurti[6] measured the scattering of light by agar sols and gels by a photometric arrangement and concluded that the micelles in gels are much bigger than those in sols. Arsiz[7] also studied the intensity of light scattered by glycerol sol of gelatin by means of photographic method.

The transparency method was first employed by Mukherjee and Majumdar[8] in the study of sols undergoing coagulation. A beam of light of constant intensity was allowed to fall on a transparent cell containing the coagulating mixture and the intensity of the transmitted light was measured by means of a thermopile connected to a galvanometer. Changes in the deflection of the galvanometer were taken to represent directly the changes

[1] *Zeit. physikal Chem.*, 1915, **89**, 186; *J.C.S.*, 1916, **109**, 1734.
[2] *Zeit. Physik.*, 1916, **17**, 557; *Zeit. Physikal Chem.*, 1917, **92**, 123.
[3] *J.C.S.*, 1920, **17**, 156.
[4] *J. Indian Chem. Soc.*, 1933, **10**, 509.
[5] *Ibid.*, 1936, **13**, 141, 309; 311.
[6] *Proc. Roy. Soc.*, 1928, **25**, 377.
[7] *Koll. Chem. Beih.*, 1915, **7**, 19.
[8] *J. Indian Chem. Soc.*, 1924, **125**, 785.

taking place in the sol. This method was employed later for the study of the kinetics of coagulation of sols and of setting of gels.[9]

Desai and co-workers[10] modified this method by employing a photocell instead of the thermopile. They obtained an important result that the coagulation velocity curves of thorium hydroxide sol could be smooth or 'S'-shaped according as the sol is highly or slightly dialysed.

In the present investigation the photocell method of Desai and co-workers has been improved as described below and has been employed to study the course of (*i*) coagulation of concentrated sols of zirconium and stannic hydroxides and (*ii*) gelation of stannic phosphate and zirconium hydroxide gel-forming mixtures.

Experimental

Description of the Apparatus.—

Light from a cinema projector lamp 120 watts, 230 volts, working at a constant current was allowed to fall on an optical cell containing the coagulating or the gelating mixture under investigation. The incident light was rendered parallel by passing through a condensing lens and the heat rays were cut off by passing the light through a cell in which water was kept circulating.

Light transmitted through the optical cell was allowed to fall on an Osram Cæsium Photo Cell enclosed in a wooden box which was covered with black paper and in which no stray light was allowed to enter. The current generated in the photocell was magnified by a single stage amplification unit and was measured by means of a galvanometer connected in the circuit. Differences in galvanometer deflections noted at different intervals of time after the coagulation or gelation has commenced, are taken as proportional to the opacity of the coagulating or the gelating mixture. The amplifying arrangement was used particularly with a view to magnify even the smallest changes which may be taking place in a sol or a gel during coagulation or gelation. Constancy of the initial reading of the galvanometer with initial dark current and also with the light falling directly on the photocell was checked from time to time during the period of observation. The reproducibility of the results was ascertained before the apparatus was employed for final readings. The whole apparatus was enclosed in a thermostat kept constant within $\pm 0{\cdot}02°$.

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[9] *Cf.* Prasad and Nabar, *J. Indian Chem. Soc.*, 1933, **10**, 53; Mehta and (Miss) Joseph, *ibid.*, 1933, **10**, 177; Prasad and Hattiangadi, *ibid.*, 1929, **6**, 653; Joshi and Rao, *ibid.*, 1936, **13**, 311.

[10] *Trans. Farad. Soc.*, 1928, **18**, 24.

(A) *Preparation of Sols.*—

(*i*) *Zirconium hydroxide.*—A concentrated sol of zirconium hydroxide was prepared by the method of Sharma and Dhar.[11] 52 g. of pure zirconium nitrate were dissolved in twice distilled water and the solution was made to 500 c.c. After 15 days of continuous dialysis of this solution a fairly concentrated sol was obtained. A portion of this sol was taken out and stored in a Jena glass flask and was used for the investigation. The zirconium contents of the sol were found to be 0·06042 moles of zirconium oxide per litre.

(*ii*) *Stannic hydroxide.*—Dhar and Varadanam's method[12] was followed for the preparation of a concentrated sol of stannic hydroxide. About 55 g. of Merck's pure stannic chloride were dissolved in 100 c.c. of distilled water and Merck's extra pure liquor ammonia was added to the solution drop by drop with constant stirring, the solution being kept cool throughout. The precipitate formed was washed free from the electrolytes and about 600 c.c. of distilled water were added to it. The stannic hydroxide was brought in colloidal form by the addition of Merck's pure ammonium hydroxide to the suspension kept continuously stirred by a glass stirrer. On standing overnight a clear sol was formed. A portion of this sol was taken out and stored for the experimental investigation. The SnO_2 contents of the sol were found to be 0·4725 moles per litre.

Experimental Procedure.—

The coagulating mixtures were prepared by mixing 1·5 c.c. of the sol diluted to 2·5 c.c. by the addition of distilled water, with a known volume of the coagulator solution, also diluted to 2·5 c.c. Test-tubes containing the two solutions were kept at constant temperature for sufficient time to acquire the temperature of the thermostat and the contents were then mixed in a definite manner. The method of mixing was maintained constant throughout. Readings were recorded at definite intervals. Unless otherwise stated white light was used as the source.

(B) *Preparation of Gels.*—

(*i*) *Stannic phosphate gels.*—Gels of stannic phosphate were prepared in the same manner as described by Prasad and Modak.[13] The concentrations of the solutions employed were also the same, *i.e.*, the solution of stannic chloride was 0·4725 N with respect to SnO_2 content and that of phosphoric acid was 0·2 N. The gel-forming mixtures were prepared from different volumes of these two solutions in the same manner as described in the case of zirconium hydroxide gels.

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[11] *J. Indian Chem. Soc.*, 1932, **9**, 455.
[12] *Ibid.*, 1936, **13**, 602.
[13] *Proc. Ind. Acad. Sci.*, 1940, **11**, 282.

(*ii*) *Zirconium hydroxide gels.*—Gels of zirconium hydroxide have been prepared by Sharma and Dhar[14] and also by Prakash.[15] The latter method which was followed in the present investigation, consists in mixing solutions of sodium acetate and zirconium nitrate of suitable concentrations in proper proportions. A ten per cent. solution of zirconium nitrate was made in distilled water and was stored in a Jena glass flask and used throughout the investigation. Solution of sodium acetate used was 3·84 N.

A known volume (x) of zirconium nitrate solution was taken in a test-tube and distilled water was added to it to make the volume to 5·0 c.c. In another test-tube a suitable volume of sodium acetate solution (y) was taken and it was also diluted to 5·0 c.c. The contents of the two tubes were mixed and the readings were taken in the same manner as described above.

Results obtained are shown graphically in which the ordinate represents the deflection differences ($di - df$) where di is the initial deflection and df the deflection at time t (expressed in minutes), in centimeters.

Fig. 1 shows the opacity changes during the coagulation of zirconium hydroxide sol with different amounts of 2·5 N solution of KCl.

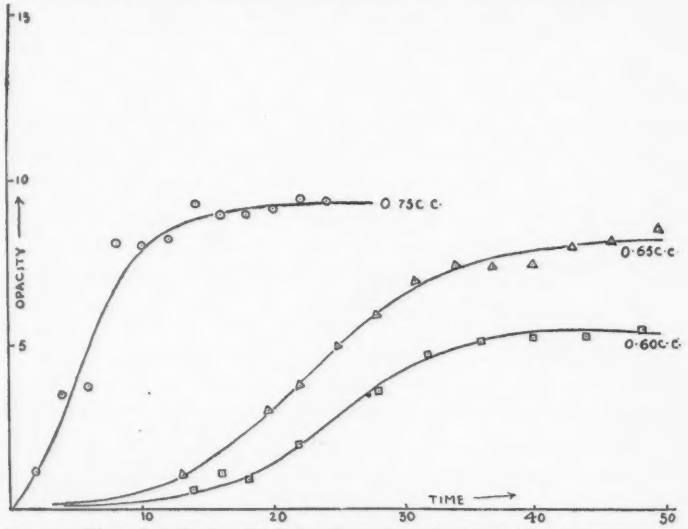

FIG. 1. Zirconium Hydroxide Sol. Coagulator KCl (2·5 N). Temperature 33°.

Fig. 2 shows the opacity changes during the coagulation of stannic hydroxide sol with different amounts of 2·15 N solution of KCl and Fig. 3 with different amounts of 0·037 N solution of $HgCl_2$.

[14] *Loc. cit.*

[15] *J. Indian Chem. Soc.*, 1932, **9**, 193.

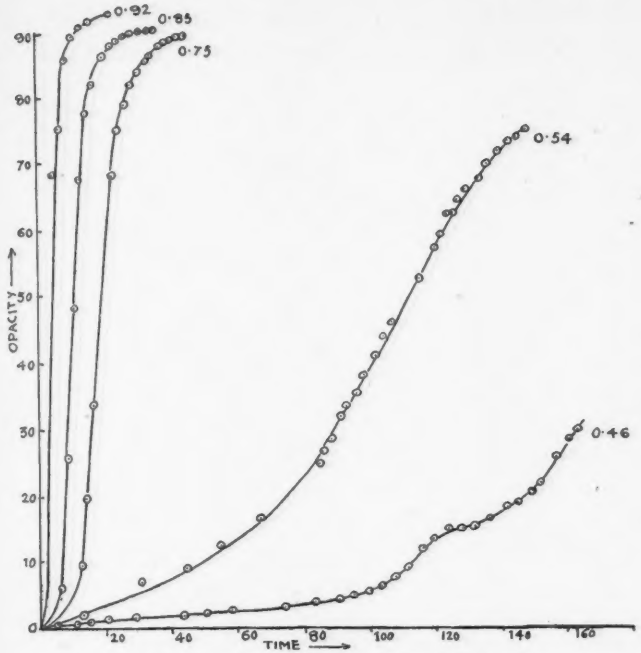

FIG. 2. Stannic Hydroxide Sol. Coagulator KCl (2·15 N). Temperature 33°.

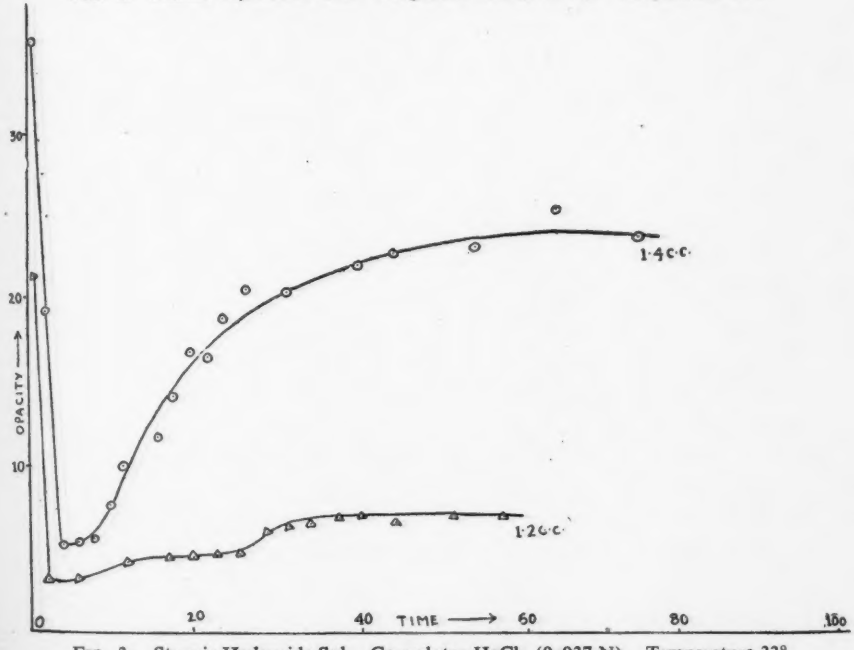

FIG. 3. Stannic Hydroxide Sol. Coagulator $HgCl_2$ (0·037 N). Temperature 33°.

Figs. 4 and 5 give the opacity changes in stannic phosphate gels containing different amounts of solutions of phosphoric acid (A) and stannic

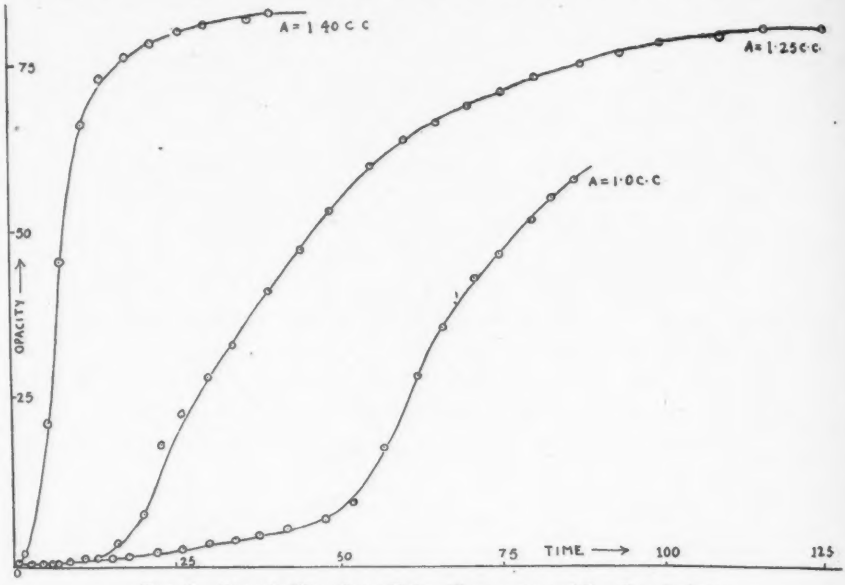

FIG. 4. Stannic Phosphate Gels. Temperature 35°. B = 1·5 c.c.

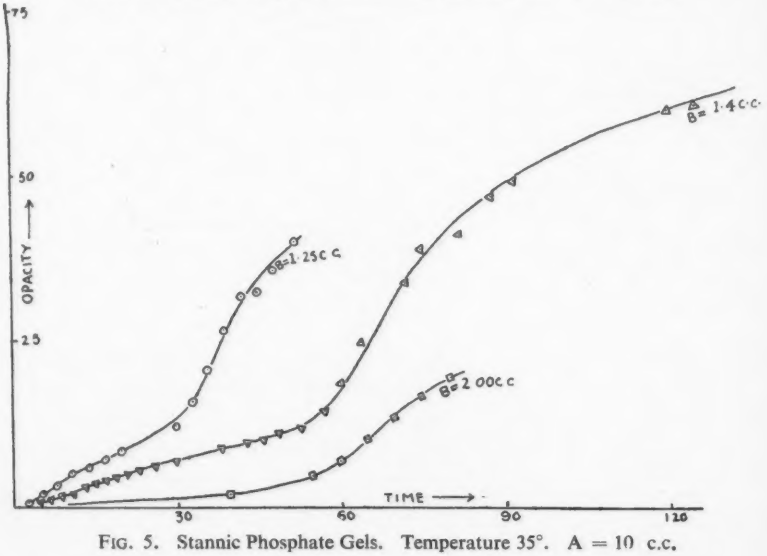

FIG. 5. Stannic Phosphate Gels. Temperature 35°. A = 10 c.c.

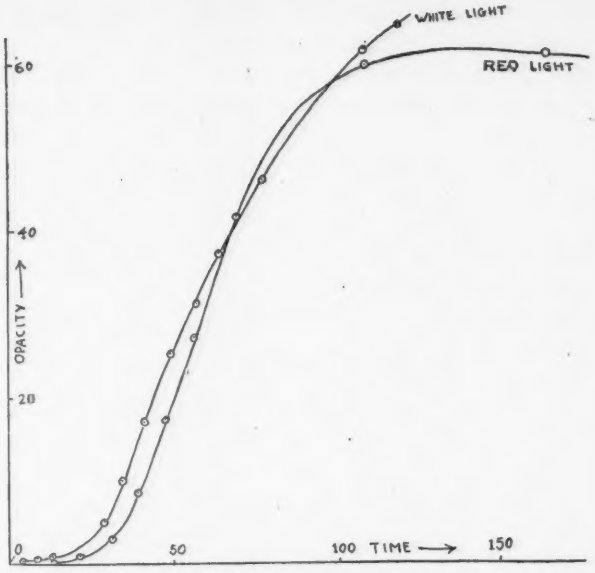

FIG. 6. Effect of Nature of Light. Temperature 35°. A = 1·20 c.c.; B = 1·75 c.c.

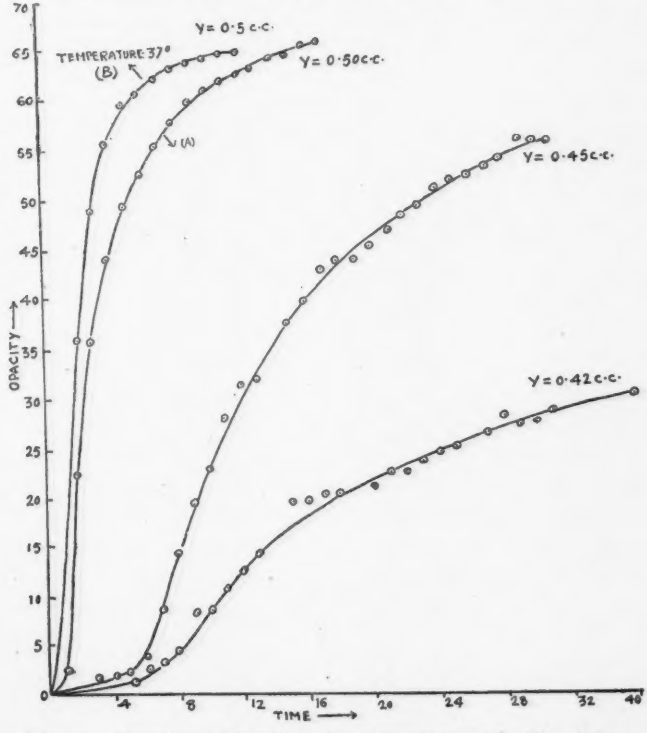

FIG. 7. Zirconium Hydroxide Gels. Temperature 33°. X = 3·0 c.c.

chloride (B). Fig. 6 shows the effect of change in the nature of incident light on the time-opacity relation with a mixture containing 1·2 c.c. of stannic chloride and 1·75 c.c. of phosphoric acid solution. The red light was obtained by introducing a red gelatin filter (610–715 $\mu\mu$) obtained from the Kodak Company.

Fig. 7 gives the opacity-time curves during the setting of zirconium hydroxide gels containing X = 3 c.c. of zirconium nitrate solution and different amounts of sodium acetate solution (Y). In this figure curve B is obtained at 37° and depicts the effect of temperature on the opacity-time relation of a gel containing 3·0 c.c. of zirconium nitrate solution and 0·50 c.c. of sodium acetate solution. Curves 1, 2 and 3 correspond to 33°.

Discussion of Results

The striking feature of all the opacity curves during coagulation shown in Figs. 1 and 2 is that they are S-shaped. In the case of both the zirconium and stannic hydroxide sols coagulated by potassium chloride, the opacity rises at first slowly, then rapidly and again slows down in the later stages. Higher concentrations (0·75 c.c.) of the coagulator seem to produce a sudden rise in the early stages of the coagulation of zirconium hydroxide sol (Fig. 1) and the S-shape of the curve is also not so perfect as in the presence of 0·60 c.c. and 0·65 c.c. of the coagulator. In the case of stannic hydroxide sol the opacity curves in the presence of larger amounts of the coagulator are very regular and steep rising but in the presence of smaller amounts they are not so smooth.

The opacity-time curves obtained during the coagulation of stannic hydroxide sol by $HgCl_2$ solution (Fig. 3) are very peculiar and very different from those shown in Figs. 1 and 2. In this case the opacity produced is very great in the beginning and decreases equally rapidly so that in about two or three minutes it comes down to a very low value. It then rises in the usual manner in the presence of 1·4 c.c. and the curve obtained is an S-shaped one while in the presence of 1·2 c.c. of $HgCl_2$ solution the opacity developed is not as much and the curve is also definitely irregular or zonal.

Opacity-time curves obtained during the gelation of stannic phosphate gel-forming mixtures are also S-shaped and appear to show the autocatalytic nature of the gelation process. These curves are either flat or rising S-shaped, depending upon the amounts of phosphoric acid and stannic chloride contained in the gel-forming mixtures. Increase in the amount of phosphoric acid increases the rate of rise in opacity; the curves in the presence of 1·00 c.c. and 1·25 c.c. of phosphoric acid are S-shaped while the one corresponding to 1·4 c.c. (Fig. 4) is practically a rapidly rising one. If coagulation precedes

the actual formation of specific structures, which is a characteristic of gel state alone, it would appear that the curves with lower phosphoric acid content indicate slow coagulation of the sol of the gelling substance and those containing larger amounts indicate rapid coagulation. These observations point out that at any time after mixing the gel-forming constituents the density of charge on the micelles in the gel-forming mixture containing 1·0 c.c. of phosphoric acid is comparatively greater and their number and their degree of hydration smaller than in mixtures which contain 1·25 c.c. and 1·40 c.c. of phosphoric acid. Same conclusions have been drawn from the measurements of viscosity made during the gelation of stannic phosphate gel-forming mixtures, containing different amounts of phosphoric acid.[16]

The rate of rise of opacity decreases with an increase in the amount of stannic chloride in the gel-forming mixtures. Assuming that the amount of stannic phosphate formed in the gel does not greatly increase, the slowing down of the gelation process on increasing the quantity of stannic chloride appears to be due to the increase in the degree of dispersity and the density of charge on the micelles and this may have been brought about by the increased preferential adsorption of the stannic ions by the colloidal particles. These results further indicate that the slowing down of gelation (possibly the coagulation which precedes it) process can be achieved by increasing the concentration of the peptising ions which increase the degree of dispersity and the density of charge on the micelles.

The increase of opacity with time may be assigned to an increase in the number and size of the micelles. When the opacity changes become minimum or the opacity reaches a constant value, the changes in the above-named factors also become minimum or come to a stop. Prasad and Hattiangadi[17] have considered this condition to be the criterion of setting of gels and have employed this method for determining the time of setting of silicic acid gels. The opacity-time curves shown in Figs. 4 to 5 can be employed also to determine the time of setting of stannic phosphate gels. The importance of such a method for determining the time of setting of a gel has been pointed out by Prasad and Parmar.[18]

The increase of the opacity of the gel-forming mixtures, at any time after the formation of gels has commenced, on increasing the phosphoric acid contents of the mixtures may have been caused also on account of all the three factors mentioned above. However, the decrease in opacity observed

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[16] *Cf.*, Prasad and Modak., *loc. cit.*
[17] *J. Indian Chem. Soc.*, 1929, **6**, 653.
[18] *Curr. Sci.*, 1935, **4**, 310.

with an increase in the stannic chloride content is mostly due to the increase in the size of the micelles, since the amount of stannic phosphate in colloidal condition cannot increase with decrease in the quantity of stannic chloride in the gel-forming mixture.

The opacity-time curves obtained with different sources of incident light (Fig. 6) are very nearly the same; the red filter having no particular advantage on the sensitivity of the method as compared to white light.

Zirconium hydroxide gel-forming mixtures appear to behave similarly to those which give rise to stannic phosphate gels. The opacity-time curves are definitely S-shaped in the presence of small amounts of sodium acetate and become rapidly rising ones (Fig. 7) when sodium acetate content of the mixture is increased. The curves with 0·42 c.c. and 0·45 c.c. appear to correspond to slow and the third one to the rapid coagulation. The increase in the opacity produced by the addition of increasing quantities of sodium acetate at any time after mixing the constituents is due to the increase in the number and the size of zirconium hydroxide micelles. These results are similar to those obtained with the stannic phosphate gel-forming mixtures to which increasing quantities of phosphoric acid are added.

It should, however, be noted that there is a distinct difference in the modes of the formation of zirconium hydroxide and stannic phosphate gels. Stannic phosphate is formed by the direct interaction of the constituents while this does not happen in the formation of zirconium hydroxide.

The opacity-time curves for the mixtures containing 3 c.c. of zirconium nitrate and 0·50 c.c. of sodium acetate solution obtained at 33° and 37° (Curves A and B, Fig. 7) are similar to each other but the curve at 33° lies lower than the curve at 37°. This may have been caused by (*i*) an increase in the number of micelles in the mixture due to increased hydrolysis with rise in temperature or (*ii*) an increase in the size of micelles, probably due to increased rate of coagulation at higher temperature or (*iii*) both.

In conclusion it may be mentioned that the optical results on the whole fail to show any distinct differences between the processes of coagulation and gelation. The distinct stages of gelation, often stated as three independent processes, fail to show their individual existence and as a whole the gelation process appears to be smooth. The fact that coagulation is the first step in the complex process of gelation may be responsible for the evidently similar curves for coagulation and gelation, the latter two steps failing to produce a marked effect on the opacity.

PRESSURE UNDER A FLUSH FLOOR WITH INCLINED SHEET PILES

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Received July, 10, 1940

Introduction

In a series of investigations carried out in connection with the design of weirs on permeable foundations, the authors have studied the problem of the uplift pressure by the electrical analogy method developed by them.[1] The results of these investigations have already been published.[2,3]

The earlier studies were concerned only with sheet piles at right angles to the floor. In the construction of the Kalabagh Weir in the Punjab, certain difficulties might be experienced in driving the sheet piles vertically downwards. An investigation of the problem of the distribution of uplift pressure under a floor with inclined sheet piles was, therefore, made. This problem was investigated by the electrical analogy method referred to above.

Experimental

In the present investigation five different inclinations (105°, 120°, 135°, 150° and 165°) of the sheet pile to the floor were studied. The length of the impervious flush floor was kept constant at 12 inches for all the cases but for every inclination of the sheet pile to the flush floor six different lengths (1″, 2″, 3″, 4″, 5″ and 6″) of sheet piles were examined. Equi-pressure lines were plotted for only three inclinations, *viz.*, 120°, 135° and 150°. For inclinations of 105° and 165° only the pressures at the points corresponding to B and C in Fig. 1 were observed. The position of the sheet piles inclined to the flush floor at the various angles investigated is shown in Fig. 1.

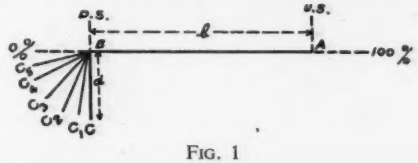

Fig. 1

The results of these investigations are represented by Figs. 2–7 and Table I, which give the pressures at B and C for the various cases.

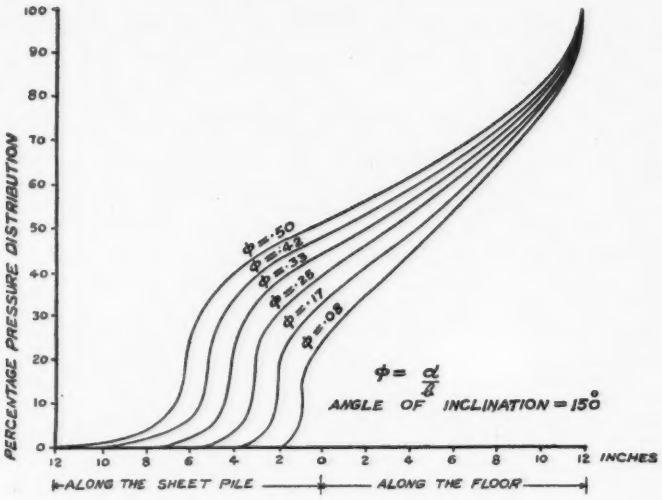
PERCENTAGE PRESSURE DISTRIBUTION
100
90
80
70
60
50
40
30
20
10
0
φ=·50
φ=·42
φ=·33
φ=·25
φ=·17
φ=·08
φ = α/d
ANGLE OF INCLINATION = 150°
12 10 8 6 4 2 0 2 4 6 8 10 12 INCHES
ALONG THE SHEET PILE
ALONG THE FLOOR

FIG. 2

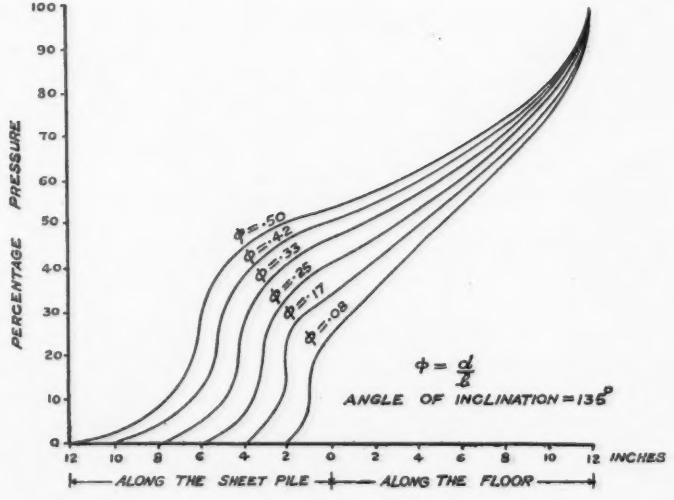
PERCENTAGE PRESSURE
100
90
80
70
60
50
40
30
20
10
0
φ=·50
φ=·42
φ=·33
φ=·25
φ=·17
φ=·08
φ = α/d
ANGLE OF INCLINATION = 135°
12 10 8 6 4 2 0 2 4 6 8 10 12 INCHES
ALONG THE SHEET PILE
ALONG THE FLOOR

FIG. 3

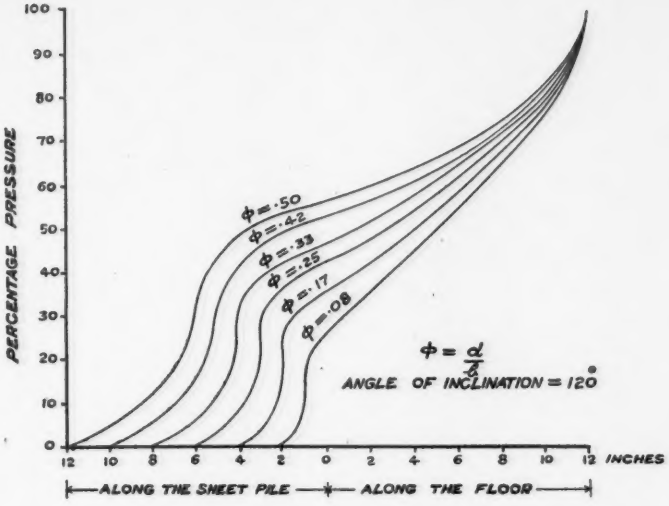
PERCENTAGE PRESSURE
100
90
80
70
60
50
40
30
20
10
0
φ=·50
φ=·42
φ=·33
φ=·25
φ=·17
φ=·08
φ = d/d
ANGLE OF INCLINATION = 120°
12 10 8 6 4 2 0 2 4 6 8 10 12 INCHES
ALONG THE SHEET PILE
ALONG THE FLOOR

FIG. 4

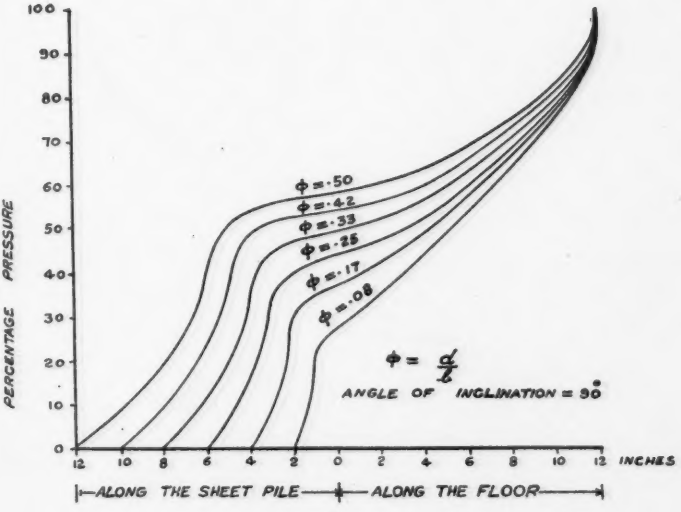
PERCENTAGE PRESSURE
100
90
80
70
60
50
40
30
20
10
0
φ=·50
φ=·42
φ=·33
φ=·25
φ=·17
φ=·08
φ = d/d
ANGLE OF INCLINATION = 90°
12 10 8 6 4 2 0 2 4 6 8 10 12 INCHES
ALONG THE SHEET PILE
ALONG THE FLOOR

FIG. 5

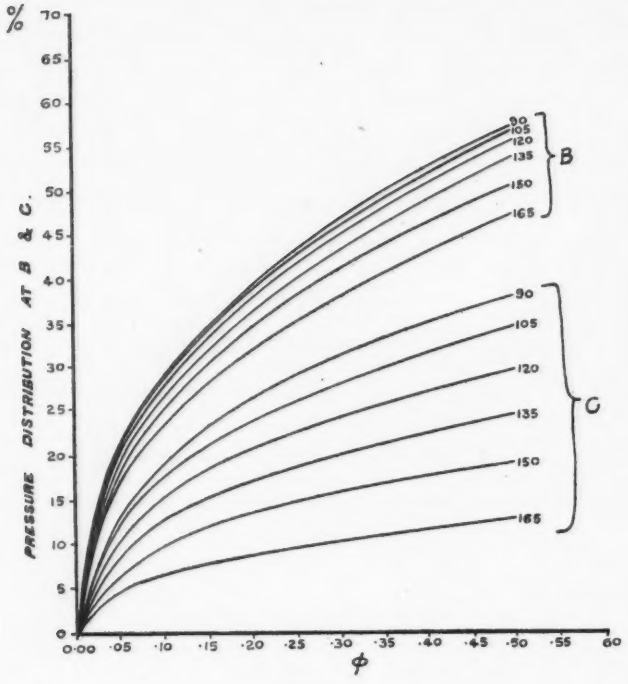
%
PRESSURE DISTRIBUTION AT B & C.
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
90
105
120
135
150
165
B
C
0·00 ·05 ·10 ·15 ·20 ·25 ·30 ·35 ·40 ·45 ·50 ·55 60
φ

FIG. 6

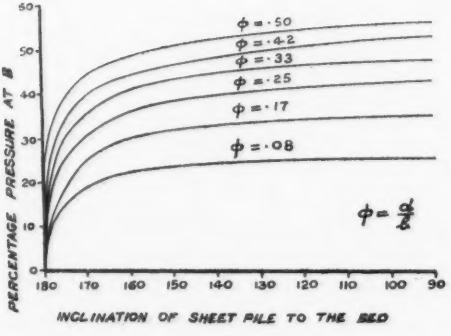
PERCENTAGE PRESSURE AT B
φ = ·50
φ = ·42
φ = ·33
φ = ·25
φ = ·17
φ = ·08
φ = d/s
180 170 160 150 140 130 120 110 100 90
INCLINATION OF SHEET PILE TO THE BED

FIG. 7

TABLE I

Depth of Sheet Pile	Percentage pressures at B and C											
	165°		150°		135°		120°		105°		90°	
	C	B	C	B	C	B	C	B	C	B	C	B
1″	6·3	21·6	9·1	23·4	11·6	24·6	14·0	25·4	16·3	25·7	17·2	26·1
2″	8·1	29·4	12·0	31·8	16·0	33·7	18·9	35·1	22·1	35·7	25·0	36·2
3″	9·7	35·0	14·8	38·2	18·8	40·0	22·7	41·8	26·4	42·7	28·5	43·2
4″	11·0	39·8	16·5	43·0	21·1	45·2	25·5	47·4	29·6	48·3	32·5	48·8
5″	12·0	43·8	18·1	47·3	23·5	50·1	28·0	52·1	32·5	53·2	35·8	53·7
6″	13·0	47·5	19·5	51·0	25·0	54·0	30·0	56·1	34·3	57·2	38·5	57·6

Fig. 2 represents the results of experiments carried out with a floor of length 12 inches and sheet piles of length 1 inch to 6 inches. The ratio d/b where d is the length of sheet piles and b is breadth of the floor is denoted by ϕ. The position of the sheet piles is at an angle of 150° to the floor. In this figure the abscissa represents the length along the floor and sheet pile and the ordinate represents the distribution of percentage pressure.

Figs. 3, 4 and 5 are plotted similarly as Fig. 2 but with angles 135°, 120° and 90° respectively between the sheet pile and the floor.

Fig. 6 represents the pressures at the points B and C (the positions of B and C are shown in Fig. 1) for various inclinations, shown in the figure, plotted against $\phi = d/b$.

Figs. 7 and 8 show the relation between the inclination of the sheet pile to the floor and the percentage pressure at B and C (the positions of B and C

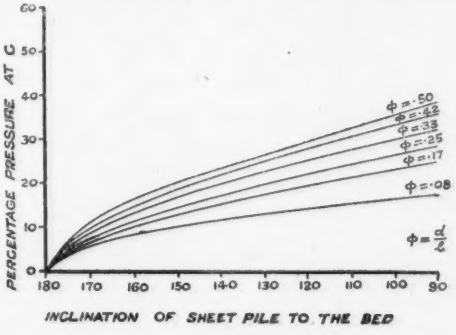

FIG. 8

are shown in Fig. 1) for various values of ϕ shown in the figure. Thus, if in a particular weir the length of the floor is 120 feet and that of the sheet pile 10 feet, ϕ will be $= \cdot 08$. If the angle of inclination is equal to 130°, then the percentage pressure at $B = 25 \cdot 2$ as can be read from curve $\phi = \cdot 08$ in Fig. 7. The pressure at C is equal to $12 \cdot 8$ as can be seen from curve marked $\phi = \cdot 08$ in Fig. 8.

A comparison of Figs. 2 to 5 shows that the pressure distribution along the floor does not show any marked change with change of inclination of sheet pile to floor. But as the angle of inclination increases, the percentage pressure at the point C, *i.e.*, the end of the sheet pile, shows a considerable decrease which means that the exit gradient decreases with the increase in inclination.

Summary

In this investigation, the distribution of uplift pressure under weirs with a single sheet pile inclined to the floor has been determined.

Five sets of experiments have been carried out, with angles of inclination of the sheet pile to the floor at 165°, 150°, 135°, 120° and 105°. In each of the sets, the pressure distribution was determined for six values of ϕ, *i.e.*, the length of sheet pile/the breadth of the floor.

In conclusion we have great pleasure in thanking Dr. E. McKenzie Taylor, the Director of Institute, for his keen interest in the problem. We have also to thank Dr. R. R. Bajpai of the Institute for his valuable assistance during the course of the investigation.

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CHEMICAL EXAMINATION OF THE ESSENTIAL OILS DERIVED FROM *ANETHUM SOA* ROXB. OIL FROM THE GREEN HERB AND THE SEEDS

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Anethum soa Roxb. is an annual glabrous herb belonging to the Natural Order of Umbelliferæ. It is commonly known as "Soa ka sag" in Hindi and "Solfa" in Bengali. It occurs throughout the tropical and subtropical India. It is avilable in the vegetable market chiefly in the months of January, February and March. For the most part it is used for culinary purposes and as a condiment. To a certain extent it is also used for medicinal purposes.

According to Dymock,[1] the leaves moistened with oil are used as a stimulating poultice or suppurative. Mahometan writers describe it as resolvent and obstrient, carminative, diuretic and emmenagogue.

The herb is strongly scented, but its aroma is not very nice or pleasant. It imparts a good flavour to the vegetables with which it is cooked and it is on this account that it finds a good market. The herb has a height of 6 inches to 3 feet, but the aroma of the plant is most when it is about 6 inches to 1 foot high and is very leafy. The stems do not contain much smell and as the herb grows taller and the proportion of stems increases, the aroma becomes less and consequently its value as an aromatic herb becomes considerably diminished. When the herb flowers, it loses its value as an aromatic herb altogether, and is then not cut down, but retained in the fields for the purpose of getting the seeds. When the seeds begin to appear, the leaves do not remain on the plant except a few here and there and the stems become rather hard.

Although the herb is very common in the Indian markets and is valued only for its aroma, it is rather queer that it has not yet been used for extracting the essential oil even on an experimental scale in India. In Europe there is a similar but not identical variety of herb known as *Anethum graveolens*, growing in Militz, which was examined by Schimmel & Co.[2] They obtained from it 0·116 per cent. of a pale green oil, the stale odour of which was entirely different from dill seed oil ($D_{15}^{\circ} = 0{\cdot}8752$; $\alpha = +108°35'$; $n^{20°} = 1{\cdot}4769$). It was soluble in an equal volume of 90 per cent. alcohol, but on the other

hand even 10 volumes of 80 per cent. alcohol were insufficient for solution. The chief constituent of the oil was found to be *d*-phellandrene, whereas carvone appeared to be not present at all. With sodium sulphite about 40 per cent. of the material reacted which when liberated from the sulphite combination had an odour of fatty aldehydes rather than that of carvone.

Dill herb oil which was distilled from the fresh herb of *Anethum graveolens* L. in Russia with an yield of 0·56 to 1·5 per cent. (referred to the dry weight of the material), possessed according to Tschernchin[3], the following constants : D = 0·8724; $\alpha = +64°35'$; $n = 1·481$; carvone content = 15 per cent.

As regards the Indian variety known as *Anethum soa*, the oil from the seeds only has been examined by Rao, Sudborough and Watson[4] and they have only determined the physical and chemical constants of the oil.

The fresh green herb examined by us on steam distillation gave a green essential oil with a disagreeable smell having the following constants :

	per cent.	
Yield	0·062	(referred to the fresh herb).
Specific gravity (20°C.)	0·8726	
Refractive index (20°C.)	1·4867	
Optical rotation (28°C.)	+286·6°	
Acid Value	2·10	
Ester value	6·72	
Saponification value	8·82	
Saponification value after acetylation ..	37·80	
Formylation value	4·90	
Total aldehydes calculated as citral and estimated by the hydroxylamine method ..	1·3	
Carvone content	Nil	
$C_{10}H_{18}O$ from Sap. Value	3·15	
Alcohols in the original oil calculated on the basis of Sap. Value after acetylation ..	10·76	

A careful examination of the oil showed that it contains a high percentage of α-phellandrene and small proportions of eugenol, iso-eugenol, thymol and phellandral.

The seeds of *Anethum soa* have a high medicinal value, and their therapeutic importance is chiefly due to the essential oil contained in them. According to Dymock,[5] an infusion of the seeds is given as a cordial drink

to women after confinement. Mahometan writers describe it as a resolvent and deobstrient, carminative, diuretic and emmenagogue.

According to Kanny Lal Dey,[6] the oil, essence and water of dill are much esteemed in India as carminative for flatulence in children and in adults.

In his *Pharmacographica Indica*, Dymock[7] describes the chemical composition of the seeds as follows : " Dill fruit yields from 3 to 4 per cent. of an essential oil, a large proportion of which was found by Gladstone (1864–72) to be the hydrocarbon $C_{10}H_{16}$ to which he gave the name " Anethene ". This substance has a lemon-like odour, Sp. Gr. at 15°C., 0·846 and boils at 172°C. It deviates a ray of polarised light strongly to the right. Nietzki ascertained that there is however present another hydrocarbon. A third constituent of the oil of dill is in all probability identical with carvol.

According to Parry,[8] the Indian dill oil has a much higher specific gravity. The figure for this varies between 0·945 and 0·970. The optical rotation varies between +40° and + 50°. This oil contains a body isomeric with ordinary apiol from parsley oil and which has been named dill-apiol.

As a result of two test distillations, Schimmel & Co.[9] have found that the oil from the seeds of this variety is not equal to the European oil. They obtained an yield of 3 and 3·5 per cent. respectively and the characters of the oils were as follows : $D_{15}° = 0·9798$ and 0·9896; $\alpha = +47°8'$ and $+45°20'$; $n = 1·49706$ and 1·49903; soluble in 3·8 and 3·2 volumes of 80 per cent. alcohol. Carvone content of both the samples (determined with neutral sodium sulphite) was 22 per cent.

The oil from the seeds of purely Indian origin seems to have been examined by Rao, Sudborough and Watson as has already been mentioned before. They obtained an yield of 3·9 per cent. The oil has the following constants : $D_{15}° = 0·9785$; $\alpha = +47·6°$; $n = 1·4934$. Carvone content by sodium bisulphite method was 19·5 per cent. These authors however did not examine the constituents of the oil and their determination of the carvone content by sodium bisulphite is open to question as carvone is determined best by precipitating the semi-carazone or by neutral sodium sulphite.

The oil obtained in the present investigation came in two lots. In the first fractions a light oil came which floated on the top of the aqueous distillate and was syphoned off from time to time. On continuing the distillation, a heavier oil began to appear which sank to the bottom of the distillate and was removed after the entire distillation process was over. The heavier oil had of course a much higher specific gravity than any hitherto recorded, whereas the average specific gravity of the lighter and the heavier oil taken together was also more than any so far recorded. These two types of oils

that separated automatically, were examined separately. The heavier oil contained a very high proportion of dill-apiol which is the last to distil, and hence the last distillate from the seeds always deposited the oil at the bottom. The yield in this case was rather low on account of the fact that only the oil automatically separating by difference in density was collected and no attempt was made to extract the oil remaining in suspension in the aqueous distillate.

Experimental

The essential oil of Anethum soa *herb.*—400 kilos of the fresh green herb collected in several lots from a local field was submitted to steam distillation from a large copper still. The green herb was cut from above the roots and the flowering plant or the plant in buds was carefully excluded. The herb was not allowed to remain either in the fields or in the laboratory for any length of time, as otherwise much of the volatile oil is lost. The oil came out entirely in the first distillate, and therefore steam distillation was discontinued after about two hours from the time oil began to appear in the distillate. The oil floating on the top of the aqueous distillate was syphoned off from time to time, and the remaining aqueous liquid returned to the still in the subsequent charge. As only the skimmed oil was collected the yield was comparatively low.

The oil was dried over anhydrous sodium sulphate and filtered. The filtered and dried oil was submitted to distillation in vacuum under a pressure of 15 mm. and the following fractions were collected:

TABLE I

Physical Constants of the Above Fractions

Fraction No.	Boiling range °C.	Volume of distillate c.c.	Per cent. yield
1	60– 80	128	78·0
2	80–130	15	9·2
3	130–150	4	2·5
4	150–170	10	6·0
5	170 and above	2	1·2
6	Residue	4	2·5
	Loss	1	0·6

TABLE II

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 20° C.
1	0·8595	1·4695	+178·4
2	0·9464	1·4765	+ 39·5
3	1·0140	1·4900	+ 12·4
4	1·1173	1·5115	+ 6·7
5	1·0754	1·5035	..

Fraction No. 1 was refractionated under a vacu of 15 mm. and the following fractions were collected :

TABLE III

Fraction No.	Boiling range ° C.	Volume of distillate c.c.	Per cent. yield
7	60–80	118	74·6
8	82–84	2	1·7
8*a*	Residue and loss	2	..

5 c.c. of Fraction No. 7 was dissolved in 10 c.c. of low boiling petroleum ether and 5 g. of sodium nitrite in 8 c.c. of water was added to the solution, 5 c.c. of glacial acetic acid was then added in small instalments and the mixture thoroughly stirred. A white crystalline magma was formed. It was filtered on a force filter and crystallised from acetone. Two fractions were obtained, one easily soluble in acetone and crystallising in colourless prisms melting at 107°C. and the other somewhat difficultly soluble and crystallising in fine colourless needles melting at 114°C. Fraction No. 7 was therefore confirmed to be α-phellandrene, and the above mentioned crystalline derivatives to be to two isomeric nitrosites.

Fraction No. 8 gave an oxime M.P. 86°C. On account of the small quantity of the fraction, more derivatives could not be prepared and the oxime already prepared could not be further purified or analysed. But in all probability this fraction was phellandral, as the oxime of phellandral should have according to Gildemeister a M.P. of 87–88°C.

TABLE IV

Physical Constants of the Above Fractions

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 20° C.
7	0·8529	1·4675	+178·5
8	0·9414	1·4745	..

Fraction No. 8 had a strong acidic reaction on litmus paper. It partially dissolved in dilute caustic soda solution, and the alkaline liquid on acidification deposited an oily substance. The entire fraction was therefore extracted with dilute caustic soda and the portion insoluble in the liquid separated. The non-phenolic portion was submitted to distillation at the ordinary pressure and the following fractions were collected :

TABLE V

Physical Constants of the Above Fractions

Fraction No.	Boiling range °C.	Volume of distillate c.c.	Per cent. yield
9	194–198	4	3·7
10	210–215	2	1·8
11	Phenolic portion recovered after acidifying the alkaline solution	0·9	0·8

TABLE VI

Physical Constants of the Above Fractions

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.
9	0·9016	1·4700
10	0·9651	1·4775

Fraction No. 11 congealed to a mass of radiating needles on cooling in a freezing mixture and gave a benzoyl derivative melting at 104°C. It was thus identified to be iso-eugenol.

Fraction No. 3 was aldehydic in nature, but could not be identified on account of the small quantity of the liquid available.

Fraction No. 4 was also acidic, and 5 c.c. of this fraction was treated with dilute caustic soda solution. 3 c.c. of the liquid did not dissolve and was separated. The non-phenolic portion (Sp. Gr. at 20°C. = 1·1126; Refractive Index at 20°C. = 1·5185) could not be identified, but the phenolic portion isolated from the alkaline liquid on acidification gave two benzoyl derivatives. One of them remained liquid, but the other separated in fine crystals. The solid portion was filtered and recrystallised. It melted at 69°C. and was identical with benzoyl-eugenol. The liquid derivative solidified on cooling in a freezing mixture and then melted at 30-32°C. It was identified to be benzoyl-thymol. The phenolic portion in Fraction No. 4 was therefore identified to be a mixture of eugenol and thymol.

Fraction No. 5 solidified on cooling in fine needles. It gave a benzoyl derivative 104°C. and was phenolic in character. It was identified to be iso-eugenol.

Thus the essential oil from the green herb of *Anethum soa* was found to have the following composition:

	per cent.
d-α-phellandrene	74·6
Eugenol and thymol	2·4
Iso-eugenol	2·0

	per cent.
Phellandral	1·7
Unidentified	11·6
Residue and loss	7·7

Essential oil from Anethum soa *seeds.*—60 kilos of the crushed seeds were distilled in steam from a large copper still. In the beginning a light oil came over and accumulated on top of the aqueous distillate. This was removed from time to time and it constituted the ' light oil ' described further on. On continuing the distillation, a heavy oil was deposited at the bottom of the aqueous distillate and this was also collected separately. The aqueous distillate freed from the two types of essential oils was returned to the still in a subsequent charge. The oils were dried over anhydrous sodium sulphate and filtered. The physical constants of the oils were determined and are given in the following table :

TABLE VII

	Light oil	Heavy oil
1. Specific Gravity at 20° C.	0·9719	1·0573
2. Refractive Index at 20° C.	1·4905	1·5385
3. Specific Rotation at 30° C.	+38·5°	+23·6°
4. Percentage of Carvone estimated by neutral soda sulphite ..	28·0	20·6
5. Percentage of carvone determined by semi-carbazide method ..	68·1	47·5
6. Acid value	..	..
7. Saponification value ..	32·8	..

Examination of the Light Oil

260 c.c. of the oil was distilled under a press. of 15 mm. and the following fractions were collected :

TABLE VIII

Fraction No.	Boiling range °C.	Volume of distillate c.c.	Per cent. yield
1	upto 80	10	3·9
2	80– 90	30	11·5
3	90–100	18	6·9
4	100–110 (const. 104)	50	19·2
5	110–120 (const. 114)	69	26·5
6	120–130 (const. 125)	..	..
7	130–140	9	3·5
8	140–160	39	15·9
9	above 160	2	0·8
10	Residue and loss	3	1·2

TABLE IX

Physical Constants of the Above Fractions

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 36° C.
1	0·81635	1·4695	+102·4
2	0·87675	1·4715	+ 86·2
3	0·89285	1·4750	+ 71·0
4	0·92885	1·4835	+ 54·9
5	0·97905	1·4915	+ 46·3
6	0·99345	1·4965	+ 38·2
7	1·03375	1·5035	+ 29·3
8	1·13035	1·5235	+ 45·0
9	1·18875	1·5195	+ 45·3

The various fractions obtained above were refractionated several times under ordinary pressure and the fractions distilling between the same boiling range were collected together. The following set of fractions were thus obtained :

TABLE X

Fraction No.	Boiling range ° C.	Volume of distillate c.c.	Per cent. yield
11	upto 170	1	0·6
12	170–180 (const. 173–175)	22	12·6
13	180–190	5	2·9
14	200–210	11	6·2
15	210–220	24	13·7
16	220–230	77	4·0
17	230–250	7	4·0
18	250–286 (const. 285)	3	1·7
19	274–284 (const. 284)	11	6·3
20	284–290 (const. 285)	8	4·6
21	Residue and loss	6	3·4

Physical Constants of the Above Fractions

TABLE XI

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 36° C.
11	..	1·46738	..
12	0·8572	1·4683	+102·0
13	..	1·4733	..
14	0·9186	1·4823	+ 68·3
15	0·9484	1·4873	+ 65·8
16	0·9985	1·4928	+ 50·0
17	1·0477	1·5043	+ 33·3
18	1·1357	1·5203	+ 11·0
19	1·1562	1·5263	± 0·0
20	1·1720	1·5283	± 0·0

Fraction No. 11 could not be identified on account of the small quantity of the substance in hand. Fraction Nos. 12 and 13 were identified to be *d*-limonene. They gave tetrabromides having m.p. 104°C. Fraction Nos. 14 to 17 were found to be *d*-carvone. Fraction Nos. 14 and 15 were digested with neutral sodium sulphite. The residual oils were very small in quantity and no definite tests could be made but the non-ketonic fraction from fraction No. 14 had a characteristic smell of anisic aldehyde and that from 15 had a distinct smell of anethol. It was kept in a freezing mixture and fine crystals got deposited in 15 but the quantity was insufficient to admit melting point determination even. Fraction No. 16 was almost entirely pure *d*-carvone. It gave an oxime m.p. 72°C. ; a semi-carbazone m.p. 162°C. and a hydrogen sulphide compound m.p. 210°C. Similar compounds were obtained from fractions 14, 15 and 17 as well. Fraction No. 17 was also digested with neutral sodium sulphite and the non-ketonic fraction was found to be pure dill-apiol on examination. Fraction Nos. 18, 19 and 20 were identified to be dill-apiol. Each of them gave a tribromide having a m.p. 110°C.

Dill-apiol was freed from associated phenolic bodies which are present in the fractions containing this fraction by extraction with caustic soda in which dill-apiol is insoluble. This treatment is necessary in order to get the dill-apiol in a perfectly pure state. All the fractions, *viz.*, 18,19 and 20 were found to contain very small proportions of phenolic bodies. The quantities of phenolic bodies were too small to admit of any detailed examination. However the three phenolic bodies obtained from the three fractions mentioned above were benzoylated. Fraction No. 18 gave a solid benzoyl derivative and the other two fractions gave liquid benzyol derivatives. Nothing further could be done with these fractions but on account of the fact that the liquid derivatives solidified on cooling they were very likely benzoyl derivatives of Thymol. Fraction No. 18 was most probably eugenol.

The residue dissolved easily in chloroform and with difficultly in alcohol. No. solid substance could be isolated. The whole thing remained a sticky mass even after repeated solution and concentration.

Examination of the Heavy Fraction

112 c.c. of the heavy fraction was submitted to fractional distillation under a pressure of 15 mm. and the following fractions were collected :

TABLE XII

Fraction No.	Boiling range °C.	Volume of distillate c.c.	Per cent. yield
1	upto 80	3	2·7
2	80 –90	6	5·4
3	90–100	18	16·1
4	120–130	12	10·7
5	130–150	14	12·5
6	150–160	46	41·1
7	above 160	1	0·8
8	Residue and loss	12	10·7

TABLE XIII

Physical Properties of the Above Fractions

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 34° C.
1	0·8685	1·4733	+94·9
2	0·8821	1·4763	+93·5
3	0·9386	1·4873	+66·5
4	0·9830	1·5023	+38·1
5	1·0774	1·5113	+23·2
6	1·1694	1·5263	± 0·0
7	1·1694	1·5263	± 0·0

The various fractions mentioned above were refractionated under ordinary pressure and the fractions boiling within the same boiling range were collected together. The following fractions were thus obtained.

TABLE XIV

Fraction No.	Boiling range °C.	Volume of distillate c.c.	Per cent. yield
9	180–190	1·5	2·5
10	190–220	4·0	6·7
11	220–230	4·0	6·7
12	230–250	7·0	11·7
13	250–280	15·0	25·0
14	285	25·0	41·6
	Residue and loss	3·5	5·8

Physical Properties of the Above Fractions

TABLE XV

Fraction No.	Specific gravity at 20° C.	Refractive index at 20° C.	Optical rotation at 31° C.
9	0·8821	1·4758	+90·6
10	0·9184	1·4813	+70·7
11	0·9870	1·4948	+48·6
12	1·0330	1·5033	+43·5
13	1·1575	1·5203	± 0·0
14	1·1696	1·5273	± 0·0

Fraction No. 9 was identified to be *d*-limonene. It gave a tetrabromide m.p. 104°C. Fraction Nos. 10, 11 and 12 were identified to be *d*-carvone. They gave hydrogen sulphide compounds having a m.p. 210°C. ; semi-carbazone m.p. 162°C. As the fractions were small in quantities no attempt could

be made to separate the carvone by neutral soda sulphite to study the non-ketonic fraction if any. Fraction Nos. 13 and 14 were identified to be dill-apiol. Both of them gave a tri-bromide m.p. 110°C. Fractions containing dill-apiol were well shaken with caustic soda solution to extract out phenols if any present. Very small quantities were obtained on acidifying the caustic soda extracts and extracting the acidified solution with ether and evaporating off the ethereal extract. These liquids were however benzoylated. The benzoyl derivatives were liquids at ordinary temperature (39°C.) but on cooling they solidified. They were not sufficient even for melting point determination. The phenolic portions were most probably thymol.

Taking both the light and heavy oils together the main constituents of the oil can be recorded as follows :

	Per cent
d-limonene	9·0
d-carvone	46·5
dill-apiol	39·6
Anethol	in traces
Anisic aldehyde	
Eugenol	
Thymol	
Residue and loss	4·9

Summary

1. On steam distillation Soa herb gives a green oil, yield 0·062 per cent. referred to the green herb.

2. The oil has a Sp. Gr. at 20°C. 0·8726, Ref. index at 20°C. 1·4867 Opt. rot. at 28°C. + 286°·6; acid value 2·10; saponification value 8·82; saponicfiation value after acet. 37·80; formylation value 4·90; total aldehydes estimated by hydroxylamine method 1·3 per cent.

3. The oil consists of α-phellandrene, eugenol, iso-eugenol, thymol and phellandral.

4. As the oil contains a high percentage of α-phellandrene it will form a very good source for the extraction of α-phellandrene. The oil itself is very valuable.

5. The seeds of *Anethum soa* of Indian origin give on steam distillation two types of oil, one heavier and the other lighter than water, yield of the automatically separating oil being 0·474 and the other 0·825 per cent.

6. Physical constants of the seed oils are :—

Sp. Gr. at 20°C. 0·9719 and 1·0573; Ref. index at 20°C. 1·4905 and 1·5385; Opt. rot. +38·5 and +23·6 respectively.

7. The oil contains 9 per cent. *d*-limonene; 46·5 per cent. *d*-carvone; 39·6 per cent. dill-apiol and probably traces of anethol, anisic aldehyde, eugenol and thymol.

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ACTION OF PHOSPHORUS HALIDES AND THIONYL CHLORIDE ON BENZILIC ACID*

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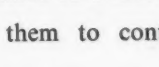
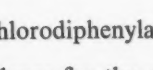
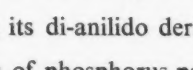
Klinger and Standke[4] who studied the reaction of phosphorus pentachloride on benzilic acid mention the reported preparation of benzilic acid chloride by Cahours as a liquid of B. P. 270° C. and state that on investigation they found that the liquid was only a mixture of benzophenone and benzophenone chloride. By the action of five moles of phosphorus pentachloride on a mole of benzilic acid they obtained a liquid which was assumed by them to contain benzilic acid chloride  in addition to α-chlorodiphenylacetic acid chloride  . They however gave no evidence for the existence of the former, although the existence of the latter was proved by them by preparing its di-anilido derivative  . Bickel[1] reports that with five moles of phosphorus pentachloride at 120–30° α-chlorodiphenylacetic acid chloride is formed.

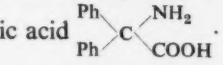
The reaction between the acid and phosphorus oxychloride was investigated by Bistrzycki and Herbst.[2] The main product of the reaction was reported to be α-chlorodiphenylacetic acid.

It is clear, therefore, that there is no definite information in chemical literature regarding the action of phosphorus pentachloride on benzilic acid. The present authors have studied the action of phosphorus halides on benzilic acid in connection with other synthetic work. In the Klinger and Standke's method (*loc. cit.*) of preparing benzilic acid amide the yield obtained is found to be small when one mole of phosphorus pentachloride is made to react with a mole of benzilic acid. This low yield is probably connected with the formation of the chloro-acid in preference to the acid chloride. Since a comparatively mild chlorinating agent like phosphorus oxy-chloride

* This paper formed part of the thesis on which Mr. S. A. Setlur was declared eligible to receive the M.Sc. Degree of the University of Bombay.

reacts only with the alcoholic –OH in the molecule leaving the carboxylic –OH unattacked, it is highly improbable that phosphorus pentachloride should first attack the carboxylic –OH.

Definite experimental evidence obtained by us indicates that phosphorus pentachloride does attack the alcoholic –OH group first. For, we have isolated α-chlorodiphenylacetic acid as the main product of the reaction in benzene solution of one mole of phosphorus pentachloride, on one mole of benzilic acid. Phosphorus oxy-chloride separates as a lower layer and is removed. It is found that no benzilic acid amide is obtained when the reaction product is treated with solid ammonium carbonate, thus indicating that no acid chloride is formed.

With excess of phosphorus pentachloride, α-chlorodiphenylacetic acid chloride is formed as evidenced by the fact that the product of reaction, on treatment with ammonium carbonate, gives benzilic acid amide in good yield. In this case the C–Cl linkage is rapidly hydrolysed to C–OH by the water present, while the –COCl is changed to $-CONH_2$ by ammonia. This is independently confirmed by the fact that the chloro acid, on treatment with ammonium carbonate and ammonia, gives almost quantitatively benzilic acid and only a very small yield of α-aminodiphenylacetic acid  .

The action of phosphorus trichloride on benzilic acid, which has not been studied hitherto, also gives α-chlorodiphenylacetic acid.

Hans Meyer[3] obtained benzophenone by the action of thionyl chloride on benzilic acid. By the action of thionyl chloride on benzilic acid in carbon tetrachloride solution at room temperature for a number of days, Stolle[5] obtained α-chlorodiphenylacetic acid. But on refluxing benzilic acid (one mole) with thionyl chloride (six moles) in carbon tetrachloride solution he obtained α-chlorodiphenylacetic acid anyhydride.

Our work confirms generally Stolle's results. We have found that a practically theoretical yield of the chloro-acid can be obtained by the action of about 1·2 moles of thionyl chloride on dry benzilic acid at room temperature, if care is taken to avoid loss of thionyl chloride.

Experimental

Action of five moles of phosphorus pentachloride on a mole of benzilic acid.—10 g. of dry benzilic acid and 50 g. of phosphorus pentachloride are ground together in a dry mortar. Within a short time a vigorous reaction starts at some point in the reaction mixture and soon spreads throughout the mixture developing heat and a copious evolution of hydrochloric acid fumes.

A liquid is formed, and the unreacted crystals of phosphorus pentachloride remain at the bottom. The supernatant liquid is transferred to a large beaker containing 60 g. of solid ammonium carbonate. The pestle is washed with a little benzene and the washings are added to the ammonium carbonate. When the vigorous reaction subsides, a little concentrated ammonia is added and the mixture is warmed on the water-bath. It is then cooled and filtered. The solid is recrystallised from choloroform. The yield is 7 g. of benzilic acid amide m.p. 153° C. On acidification the filtrate does not deposit any benzilic acid.

Action of one mole of phosphorus pentachloride on a mole of benzilic acid.—2·2 g. of dry benzilic acid and 2 g. of phosphorus pentachloride, both dissolved in benzene, are mixed together and kept overnight at room temperature in a filter flask. The greater portion of benzene is evaporated at room temperature by applying suction to the flask when the liquid is found to separate into two layers. The lower layer is of phosphorus oxychloride. The large crystals that separate from the concentrated benzene solution are found, on recrystallisation, to have a m.p. of 120° (decomp.). Yield is 1·5 g.

Action of phosphorus trichloride on benzilic acid.—2 g. of dry benzilic acid and 2 c.c. of phosphorus trichloride are mixed in a filter flask, which is then slightly warmed and kept corked overnight. Excess of phosphorus trichloride is removed by applying suction at room temperature. The residue is extracted with dry benzene. From the benzene solution crystals having m.p. 120° (decomp.) and identical with α-chlorodiphenylacetic acid separate. Yield is 1·5 g.

Action of thionyl chloride on benzilic acid.—Dry powdered benzilic acid (10 g.) is taken in a conical flask fitted with a cork carrying a tube bent twice at right angles and terminating in a calcium chloride tube. Thionyl chloride (3 c.c.) is added and the mixture shaken and kept overnight. Large crystals are formed and on washing with a little benzene-petrol mixture give m.p. 119–20° (decomp.). Yield is 10 g.

Summary

Klinger and Standke's claim of having prepared benzilic acid chloride by the action of phosphorus pentachloride on benzilic acid is untenable. Even comparatively mild chlorinating agents like phosphorus trichloride, phosphorus oxychloride and thionyl chloride react with benzilic acid replacing the alcoholic –OH by –Cl and giving α-chlorodiphenylacetic acid. The same product is obtained in benzene solution at room temperature by the action of one mole of phosphorus pentachloride on a mole of benzilic acid.

Excess of phosphorus pentachloride then reacts with the carboxylic group giving α-chlorodiphenylacetic acid chloride.

Thionyl chloride reacts with benzilic acid at room temperature giving a good yield of α-chlorodiphenylacetic acid.

The authors wish to thank Prof. R. N. Bhagvat, M.A., B.Sc., Director, Department of Chemistry, St. Xavier's College, Bombay, for his kind interest throughout the work.

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A NOTE ON THE NEGATIVE PRESSURE AND MOISTURE CONTENT OF A PUNJAB SOIL

By D. C. Midha

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(Communicated by Dr. V. I. Vaidhianathan, D.Sc., F.A.Sc.)

Introduction

It is well known that plants draw their supply of water from the soil in which they are grown. In order that plants should grow, the soil must contain enough moisture and it should be able to supply that moisture to the plants. The ability of a plant to draw water from the soil depends also upon the physical structure of the soil. A sandy soil would part with its moisture much more readily than a clay soil. As the water is drawn by the plants, a negative pressure is set up in the soil. For a certain percentage of moisture, a much greater negative pressure is developed in a clay soil than in sand. The negative pressure thus depends upon the particle size of the soil. Joffe and McLean[1] have attempted to estimate the colloidal content of a soil from the negative pressure. Rogers[2] has devised a soil moisture meter depending upon the force with which moisture is absorbed by a particular soil. Haines[3] has pointed out that there is no unique value of moisture corresponding to any one negative pressure in a soil. According to him the negative pressure depends not only on the particle size and moisture content of the soil but also upon the process by which it has been brought to that state of moisture. A falling moisture would give rise to higher pressure deficiency than that developed under conditions of increasing moisture. Rogers[2] has, however, shown that in an ordinary soil consisting of particles of mixed sizes, the error arising from irreversibility of the moisture cycle is small for practical purposes. The negative pressure (being dependent both upon the physical structure of the soil and the moisture present in it) can, therefore, be taken as an index of the ability of a soil to supply water to the plant.

A study of the various aspects of the negative pressure in soils of the Punjab has been started in the Irrigation Research Institute, Lahore. The present paper gives the negative pressures for different values of moisture present in a Punjab soil with pH 9·38. The investigation is being continued.

Experimental

If a porous vessel containing water is placed in contact with unsaturated soil, water is drawn by the soil through the pores of the vessel. A negative pressure is thus produced in the vessel which can be measured by means of a manometer connected to the porous pot.

A sketch of the apparatus used in the present experiment is shown in Fig. 1. It consists of a porous pot P closed at the bottom. The other end

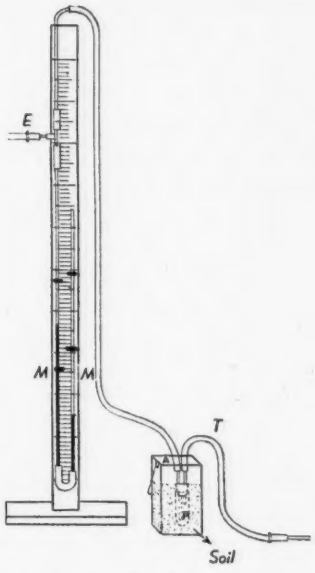

FIG. 1

has two openings. One of these is connected to a U-tube mercury manometer MM. The other opening (T) is used as an outlet for air as the apparatus is filled with water by means of the side-tube E in the manometer. When the apparatus has been filled with water free from air, the tubes T and E are closed by means of pinch-cocks. The porous pot is then embedded in the soil contained in the vessel A. As the water is absorbed by the soil, the mercury column in the manometer begins to rise and ceases when the negative pressure in the soil is in equilibrium with the pressure indicated by the manometer. The steady reading of the manometer gives the negative pressure at the particular moisture content of the soil.

After taking the final reading of pressure, three samples of the soil under examination are taken at different depths from the vessel A. They are

weighed and dried at 110° C. Their mean value is taken as the representative moisture content of the soil.

Results

The soil sample investigated had a pH value of 9·38, and contained 13·18 per cent. of clay (particles below ·002 mm.), 36·48 per cent. of silt (particles between ·002 and ·02 mm.) and 45·76 per cent. of sand (particles above ·02 mm.). The results showing the relation between negative pressure and moisture content are given in Fig. 2. As can be seen from the figure,

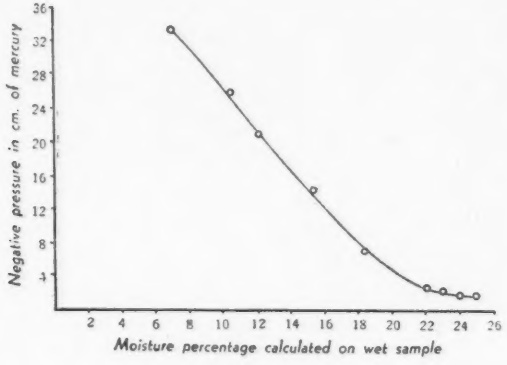

FIG. 2

the curve is almost parallel to the abscissa for moistures above 20 per cent. Between the percentage of moisture 20 and 7 the curve becomes steep. This shows that the change in negative pressure is small as the moisture content rises above 20 per cent. The change in negative pressure is much more rapid as the moisture content decreases from 20 per cent. to 7 per cent.

In carrying out these experiments it was necessary to avoid the following errors:—

(1) The effect of evaporation from the surface of the soil. In order to avoid this source of error, the porous pot was placed deep enough in the soil.

(2) The time lag in the rise of the mercury column.

It is observed that the level of mercury comes to a steady state after some time depending upon the moisture initially present in the soil. The rate of rise of mercury in the manometer at 12 per cent. soil moisture has been observed to correct this error. The observations are shown in Fig. 3. The figure shows that the rise is comparatively rapid to begin with and slows

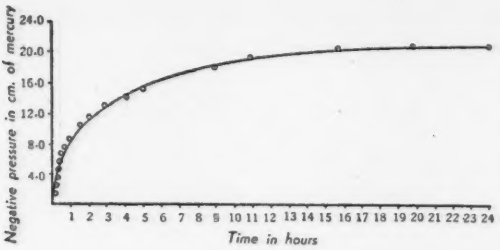

FIG. 3.

down with time. After 20 hours the curve becomes parallel to the time-axis showing that the mercury column has attained its maximum level in equilibrium with the negative pressure in the porous pot. The observations of negative pressure given in Fig. 2 were taken after 48 hours to ensure that the soil had developed its full negative pressure for that moisture content.

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CHEMOTHERAPY OF BACTERIAL INFECTIONS

Part III. Synthesis of (N^4)-Amino-substituted Heterocyclic Derivatives of Sulphanilamide

By K. Ganapathi

(*From the Haffkine Institute, Parel, Bombay*)

Received June 26, 1940

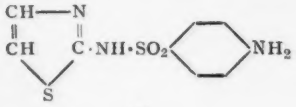
(Communicated by Lieut.-Col. S. S. Sokhey, M.A., M.D., F.A.SC., I.M.S.)

The synthesis of 2-N^1-sulphanilamidothiazol (I) and also its striking therapeutic properties in experimental plague, *streptococcal* (*hemolytic*) and *pneumococcal* infections in mice have been reported from this Institute.[1–5] The efficacy of this new drug in the other types of *pneumococcal*, *meningococcal*, *staphylococcal* and *lymphogranuloma venerum* infections has been described by many American workers.[6] There are also some preliminary reports of clinical trials of this and the related 4-methyl derivative in *pneumococcal* and *staphylococcal* infections.[7] Very significant of all these are the findings of Sokhey and Dikshit[8] that this new drug shows a striking specific therapeutic effect in plague infections far superior to 2-sulphanilamidopyridine. As a natural sequel to this important discovery, the synthesis of similar and related types of heterocyclic derivatives of sulphanilamide were undertaken with a view to giving an extensive trial to these promising classes of compounds.

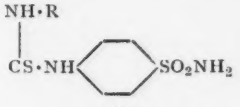
Heterocyclic derivatives of sulphanilamide can in general be of two classes according as the heterocyclic ring is substituted in the amino (N^4) or the sulphonamido (N^1) radical of sulphanilamide. It has been pointed out[1, 2] that whereas the derivatives of the first group may either be of poor activity or possess no advantage over sulphanilamide, only those of the second group may be more active and polyvalent in action than the parent sulphanilamide. The object, however, in deliberately undertaking at present the synthesis of heterocyclic derivatives of the first (N^4-amino substituted) group is (1) to verify the above conclusion and (2) to examine, in case some of them prove to be quite active, whether the toxic reactions, now associated with the free amino group of sulphanilamide and its derivatives,[9] are less intense or absent in them. In this paper, we report the synthesis of N^4-amino substituted thiazol, thiazolin, pseudothiohydantoin and acridine derivatives of

sulphanilamide undertaken with the above objective; the corresponding (N[1]) sulphonamide substituted isomers and derivatives will be described in a future communication.

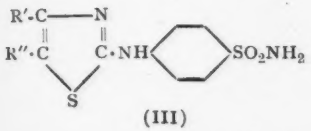
Sulphanilamide hydrochloride reacted with potassium thiocyanate to furnish N-*para*sulphonamidobenzene-thiocarbamide (II, R–H). On treating with 1 : 2-dichloroether the thiourea derivative yielded a thiazol which, by analogy, can be represented as 2-*para*sulphonamidobenzene-aminothiazol (III, $R' = R'' = H$) or its desmotropic form 2-*para*sulphonamidobenzene-iminothiazolin (IV, $R = R' = R'' = H$). On heating the above thiourea



(I)



(II)



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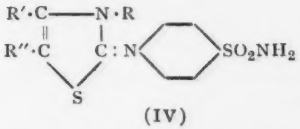
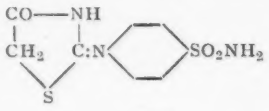


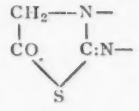
(IV)

derivative with phenacylbromide, the corresponding phenylthiazol derivative (III, $R' = Ph$, $R'' = H$) capable of existing in the desmotropic form (IV, $R = R'' = H$, $R' = Ph$) was produced. Similarly, N-*para*sulphonamido-phenyl-N′-phenyl thiocarbamide (II, $R = Ph$)[1] and N-*para*sulphonamido-phenyl-N′-allylthiocarbamide (II, R = allyl)[10] with 1 : 2-dichloroether yielded respectively 2-*para*sulphonamidobenzeneimino-3-phenylthiazolin (IV, $R = Ph$, $R' = R'' = H$) and 2-*para*sulphon-amidobenzeneimino-3-allylthiazolin (IV, R = allyl, $R' = R'' = H$). The allylthiocarbamide derivative (II, R = allyl) with phenacyclobromide furnished 2-*para*sulphonamido benzeneimino-3-allyl-4-phenylthiazolin (IV, R = allyl, R' = phenyl, $R'' = H$). Ethyl-α-bromoacetoacetate, ethyl-γ-bromoacetoacetate and ethyl-β-bromolevulinate condensed with N-*para*sulphonamidophenylthiocarbamide to yield respectively ethyl-2-*para*sulphonamidobenzeneamino-4-methylthiazol-5-carboxylate (III, $R' = CH_3$, $R'' = CO_2Et$), ethyl-2-*para*sulphonamidobenzeneaminothiazolyl-4-acetate (III, $R' = -CH_2CO_2Et$, $R'' = H$) and ethyl-2-*para*sulphonamido-benzeneamino-4-methylthiazolyl-5-acetate (III, $R' = CH_3$, $R'' = -CH_2CO_2Et$), these compounds also being capable of existing in the corresponding desmotropic forms of formula (IV). In all the above condensations, formation of thiazol or thiazolin derivatives with the *para*sulphonamidobenzene group in position 2 in preference to the position 3 is assumed only by analogy and not with any rigorous experimental proof.

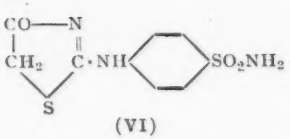
Chloracetic acid, chloraceticester or chloracetylchloride condensed with N-*para*sulphonamidophenylthiocarbamide and the compound obtained can be either N^2-*para*sulphonamidophenylpseudothiohydantoin (V or VI) or 3-*para*sulphonamidophenylpseudothiohydantoin (VII).* By analogy with the investigations of previous workers,[11] we prefer the structure (V or (VI) for this compound. Adams, Long and Jeanes[12] by treating *para*sulphonamidochloracetanilide with ammonium thiocyanate obtained a product for



(V)



(Va)



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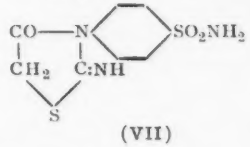
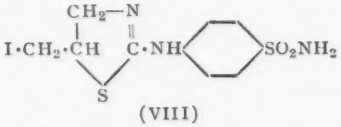
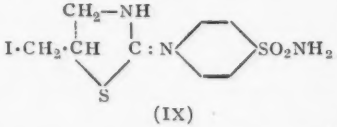


(VII)

which they have assigned the structure (VII) though there are instances in literature[13] to indicate that this compound can possess the alternative structure (V) or (VI) as well. We are not sure whether our product is identical with that of Adams *et al.* but it is of interest to note that in our experiments we could isolate some sulphanilamide evidently formed by the hydrolysis of the compound of structure (V). N-allyl-N′-*para*sulphonamidobenzenethiocarbamide on treating with iodine in alcoholic solution yielded a heterocyclic derivative which by analogy can be represented as 2-*para*sulphonamidobenzene amino-5-iodomethyl Δ^2-thiazolin (VIII) or the desmotropic thiazolidon (IX).



(VIII)



(IX)

2-Sulphanilamidothiazol (I) on being diazotised and coupled with 4-aminothiouracil yielded the dye (X); on being condensed with *para*acetaminobenzenesulphochloride and the product hydrolysed, the derivative (XI)

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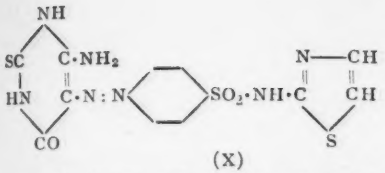
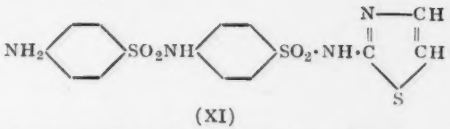
* In this reaction, compounds of the isomeric type (V*a*) do not appear to be formed. The few instances in older literature wherein such a structure has been assigned to compounds obtained by treating chloracetic acid with thiourea derivatives, should be revised. Andreasch[14] obtained a "thiohydantoin" (now to be called pseudothiohydantoin) derivative by a similar method and assigned it the now accepted structure but in Beilstein's Handbuck (Bd. XXVII, Syst. No. 4298, p. 239) it is wrongly recorded to be of type (V*a*).



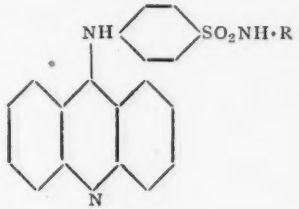
(X)



(XI)

was obtained. The gold salt of the derivative (X) and similar ones reported previously,[1] are for trial in tuberculosis.

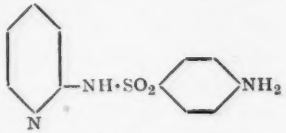
Five typical N^4-substituted sulphanilamide derivatives of acridine of formula (XII) have been synthesised by condensing 9-chloracridine with sulphanilamide, 4-sulphanilamidobenzenesulphonamide, 4′ : 4-diamino-benzenesulphoanilide, 4-amino-4′-nitrobenzenesulphonanilide and 2-sulphanilamidopyridine.



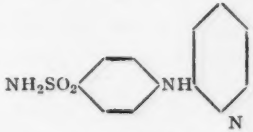
(XII)

All the thiazol, thiazolin and pseudothiohydantoin derivatives described were found to be inactive in *streptococcal* and *pneumococcal* infections in mice. The two derivatives (X) and (XI) were also inactive in *pneumococcal* infections; but they showed considerable activity in *streptococcal* infections. None of the acridine derivatives showed any *antipneumococcal* activity but a few showed considerable *antistreptococcal* activity. (The details of the animal experiments carried out in this Institute will be published elsewhere.)

The above results lend additional support to the view that for pronounced antibacterial action the heterocyclic ring should be substituted in the sulphonamide radical of sulphanilamide with the amino group being free.[1] It is thus very significant that whereas 2-sulphanilamido-thiazol (I) and 2-sulphanilamidopyridine (XIII) possess remarkable antibacterial action, the isomeric derivatives (III, $R' = R'' = H$) and (XIV)[15] are inactive.



(XIII)



(XIV)

The activity of the (N^4) amino-substituted derivatives of sulphanilamide reported till now can be traced to the sulphanilamide liberated from them *in vivo*.[1,16] The only doubtful cases is that of *para*sulphonamidophenylguanidine[17]; it is not clear whether this compound also yields sulphanilamide *in vivo* or whether the guanidine radical itself, now known to be of much significance in the chemotherapy of protozoal infections,[18] possesses some inherent therapeutic property.

It is of course tempting to suggest that the importance of the free amino group as indicated above may have some bearing on the hypotheses postulated that the activity of sulphanilamide (and possibly the other derivatives also) is due to the biologically mediated oxidation or oxidation-reduction systems involving the free amino group.[19] But very recently it has been shown that the action of sulphanilamide is due to the competitive inhibition of some vital enzyme reaction of the bacterial cell which has for its substrate the " essential metabolite", *para*aminobenzoic acid.[21] Since the inhibitory action of sulphanilamide is due to its structural similarity to the *para*aminobenzoic acid, the importance of a free amino group in the sulphanilamide derivatives is understandable.

Experimental

N-para*sulphonamidobenzenethiocarbamide* (*II*, $R = H$).—*Para*aminobenzenesulphonamide (110 g.) dissolved in water (500 c.c.) and hydrochloric acid (d. 1·19; 50 c.c.) was treated with potassium thiocyanate (60 g.) and the solution evaporated to dryness in a china-dish on the steam-bath. The residue on crystallisation from boiling water yielded the thiourea derivative in shining thin rhombic plates or leaflets, m.p. 197° (dec.); yield, 85 g. (Found: N, 18·3; $C_7H_9N_3O_2S_2$ requires N, 18·2%.)

2-(Para*sulphonamidobenzeneamino*)-*thiazol* (*III*, $R = R' = H$) or 2-para*sulphonamidobenzeneiminothiazolin* (*IV*, $R = R' = R'' = H$).—The foregoing thiocarbamide (5·7 g.) and 1 : 2-diochlorether (4 c.c.) in water (20 c.c.) were heated under reflex. After everything had gone into solution, boiling was continued for 45 minutes more. The solution was cooled and made ammoniacal whereby the thiazol derivative was precipitated. It separated from water as a greyish amorphous powder, m.p. about 240° (dec.). Yield, 5·0 g. (Found : N, 16·3; $C_9H_9N_3O_2S_2$ requires N, 16·5%.)

2-Para*sulphonamidobenzeneimino*-3-*allylthiazolin* (*IV*, $R =$ *allyl*, $R' = R'' = H$).—N-*para*sulphonamidophenyl-N′-allylthiocarbamide (5·4 g.) and 1 : 2-dichlorether (2·7 c.c.) in water (30 c.c.) were heated under reflex for 1½ hrs. The clear cooled solution was neutralised with ammonia and the solid that separated on crystallisation from alcohol was obtained in rhombic plates,

m.p. 139·5–41°, yield, 5·8 g. (Found : N, 13·6; $C_{12}H_{13}N_3O_2S_2$ requires N, 14·2%.)

2-Para*sulphonamidobenzeneimino*-3-*phenylthiazolin* (*IV*, $R = Ph$, $R' = R'' = H$).—This was prepared as above by heating equimolecular quantities of N-phenyl-N′-*para*sulphonamidophenylthiocarbamide and 1: 2-dichlorether in water ; m.p. 193°. (Found : N, 12·2; $C_{15}H_{14}N_3O_2S_2$ requires N, 12·7%.)

2-Para*sulphonamidobenzeneimino*-3-*allylthiazolin* (*IV*, $R = allyl$, $R' = Ph$ *and* $R'' = H$).—Prepared by heating equimolecular quantities of N′-*para*-sulphonamidophenyl *N*′-allylthiocarbamide and phenacylbromide in water. It crystallised from alcohol in shining prisms or plates, m.p. 209–10°. (Found : N, 11·0; $C_{18}H_{18}N_3O_2S_2$ requires N, 11·3%.)

2-Para*sulphonamidophenylamino*-4-*phenylthiazol* (*III*, $R' = Ph$, $R'' = H$) or 2-para*sulphonamidophenylimino*-4-*phenylthiazolin* (*IV*, $R = R'' = H$ $R' = Ph$).—Prepared as above by heating equimolecular quantities of phenacyl bromide and N-*para*sulphonamidophenylthiocarbamide in water or alcohol, m.p. 228–30°. (Found : N, 12·4; $C_{15}H_{14}N_3O_2S_2$ requires N, 12·7%.)

Ethyl 2-para*sulphonamidobenzeneamino*-4-*methylthiazol*-5-*carboxylate* (*III*, $R' = Me$, $R'' = CO_2Et$) *or ethyl* 2-para*sulphonamidobenzeneimino*-4-*methyl-thiazolin*-5-*carboxylate* (*IV*, $R = H$, $R' = CH_3$, $R'' = CO_2Et$).—A mixture of ethyl-α-bromacetoacetate (17 g. freshly prepared by brominating ethylaceto-acetate with one molecule of bromine at 0° C. according to the method of Conrad and Schmidt[20]), finely powdered N-*para*sulphonamidophenylthio-carbimide (18 g.) and water (200 c.c.) was warmed on the steam-bath with vigorous shaking. The mass gradually turned yellow and shaking was con-tinued till the smell of the ester was not perceptible. After allowing to stand overnight, it was filtered, dissolved in (2N) sodium hydroxide and the clear solution neutralised whereby the thiazol ester separated. It was filtered and on crystallisation from dilute alcohol was obtained as light yellow prisms, m.p. 243–45°, yield, 25 g. (Found : N, 11·9 ; $C_{13}H_{15}N_3O_4S_2$ requires N, 12·3%.)

Ethyl 2-para*sulphonamidobenzeneaminothiazolyl*-4-*acetate* (*III*, $R' = -CH \cdot COEt$, $R'' = H$) *or* 2-para*sulphonamidobenzeneiminothiazolinyl*-4-*ethylacetate* (*IV*, $R = R'' = H$, $R' = -CH_2CO_2Et$).—This was prepared as the foregoing by condensing N-*para*sulphonamidopnenylthiocarbamide with an equi-molecular quantity of ethyl-γ-bromoacetoacetate (prepared by brominating ethylacetoacetate in carbon disulphide at room temperature[20]). It was obtained as a yellowish brown crystalline powder, m.p. 219–20° (slight dec.). (Found : N, 12·2; $C_{13}H_{15}N_3O_4S_2$ requires N, 12·3%).

Ethyl 2-para*sulphonamidobenzeneamino-4-methylthiazolyl-5-acetate* (*III*, $R' = Me$, $R'' = -CH_2 \cdot CO_2Et$) *or Ethyl* 2-para*sulphonamidobenzeneimino-4-methyl thiazolinyl-5-acetate* (*IV*, $R = H$, $R' = Me$, $R'' = -CH_2 \cdot CO_2Et$).—Finely powdered N-*para*sulphonamidobenzenethiocarbamide (10 g.), ethyl-β-bromolevulinate (12·5 g.) and water (150 c.c.) were warmed on the water-bath with vigorous shaking for about 45 mts. It was then filtered, and the clear filtrate neutralised with ammonia whereby the condensation product separated. It crystallised from alcohol in shining rhombic plates, m.p. 163°, after softening at 154°, yield, 12 g. (Found : N, 11·6; $C_{14}H_{17}N_3O_4S_2$ requires N, 11·8%.)

N-para*sulphonamidophenylpseudothiohydantoin* (*V* or *VI*).—This was prepared by refluxing equimolecular quantities of chloracetic ester or chloracetic acid and N-*para*sulphonamidobenzenethiocarbamide in absolute alcohol for 2 to 3 hours. In the place of the acid or ester, chloracetyl chloride can also be used but the reaction is best conducted in acetone. It crystallised from alcohol in fine needles melting indefinitely between 240–55°. (Found : N, 15·2; $C_9H_9N_3O_3S_2$ requires N, 15·5%.)

When the reaction was carried out in dilute alcohol or water or the refluxing much more prolonged, in addition to the above product, sulphanilamide was also isolated.

2-Para*sulphonamidobenzeneamino-5-iodomethylthiazolin* (*VIII*) *or* 2-para*sulphonamidobenzeneimino-5-iodomethylthiazolidon* (*IX*).—To a solution of N-allyl-N′-*para*sulphonamidophenylthiocarbamide (5·4 g.) in absolute alcohol (50 c.c.) was added iodine (5·1 g.) and refluxed on the steam-bath. The solution was decoloursied in about 15 mts. After boiling for 2 hours more, the solution was diluted and neutralised with ammonia. The oil that separated gradually solidified. From alcohol it separated as a gum and gradually crystallised; m.p. 115–19°, yield, 4·9 g. (Found : N, 10·2; $C_{10}H_{12}N_3O_2S_2I$ requires N, 10·6%.)

4-*Amino*-5-[4′-(2) *thiazolylsulphonamidophenylazo*] *thiouracil* (*X*).—2-N^1-sulphanilamidothiazol (2·5 g.) was diazotised whereby the diazo-compound separated as a yellow mass. The excess of nitrous acid being destroyed with ammonium sulphamate, it was added to a solution of 4-aminothiouracil (1·5 g.) dissolved in sodium hydroxide (20 c.c. of 2·5 N). After stirring for about 15 mts. the dark red solution was acidified with acetic acid whereby the red dye was precipitated. It was filtered, washed well with water and dried; yield, 4 g. (Found : N, 23·4; $C_{13}H_{11}N_7O_3S$ requires N, 24·0%.)

2-(4-N^1-*sulphanilamidobenzenesulphonamido*) *thiazol* (*XI*).—To a solution of 2-N^1-sulphanilamidothiazol (5 g.) in pyridine (6 c.c.) and acetone

(20 c.c.) was added *para*acetaminobenzenesulphochloride (5 g.) and heated on the steam-bath for ½ hour. The solution was diluted with water, filtered and the solid obtained was thoroughly triturated with dilute hydrochloric acid and filtered. The product obtained was boiled with 8 times the quantity of about 3·5 N hydrochloric acid for 45 mts. and filtered. The clear filtrate was neutralised with ammonium hydroxide and the product that separated crystallised from alcohol. Greyish prisms, m.p. 163–4°. (Found: N, 13·6; $C_{15}H_{14}N_4O_4S_3$ requires N, 13·7%.)

9-*Chloroacridine*.—The methods of synthesis of this compound described in literature are lacking in details; the following method gave the compound in good yields and is fairly rapid also.

A solution of equal amounts of 2-chlorobenzoic acid and potassium carbonate was evaporated to dryness first on the steam-bath and then at 110°. The solid mass was finely powdered and then heated under reflux with three times the amount of aniline and a little copper powder for three to four hours. The product was then acidified with dilute hydrochloric acid whereby diphenylaminecarboxylic acid separated. It was filtered, dissolved in dilute sodium hydroxide, filtered and the clear filtrate acidified. The acid that separated was filtered off, washed with water and dried. This was found to be pure enough for the next operation. The foregoing dry acid with 5 to 8 times of phosphorous oxychloride was refluxed first very gently till the vigour of the reaction subsided. After refluxing for two hours it was poured into crushed ice and water, care being taken that during decomposition of the oxychloride the product did not get warmed up. After making it alkaline with ammonia at about 0° to 5°, the chloroacridine which separated and recognisable by the characteristic aromatic odour, was filtered, washed well with ice water and thoroughly dried in a *desiccator*. If in any one of the operations the temperature was allowed to rise or the wet product warmed with any solvent, the chloracridine was converted into acridone showing the blue fluorescence. The above dry chloracridine is pure enough for the subsequent operations and the dry product can be crystallised from absolute alcohol.

Acridine derivatives of formula (*XII*).—The acridine derivatives mentioned below were prepared by the following general method. One molecule of 9-chloracridine was heated on the steam-bath with 5-8 times the weight of phenol till everything went into solution. Then one molecule of the finely powdered amine ($NH_2 \cdot C_6H_4 \cdot SO_2NH \cdot R$) was added and heated on the steam-bath for two hours more with frequent shaking. The syrupy solution was then diluted with water and made just alkaline with ammonia. The

acridine derivatives separated as gums and soon solidified on scratching. They were all crystallised from alcohol.

N^4-(9′-*acridyl*) *sulphanilamide* (*XII*, $R = H$.)—Orange yellow fine needles, m.p. 245–6°. (Found : N, 12·1; $C_{19}H_{15}N_3O_2S$ requires N, 12·0%.).

2-[N^4-(9′-*acridyl*) *sulphanilamido pyridine*] (*XII*, R = 2-*pyridyl*).—Brown red plates which on powdering became orange yellow, m.p. 268–9° (dec.). (Found : N, 12·6; $C_{24}H_{18}N_4O_2S$ requires N,13·1%).

4-[N^4-(9′-*acridyl*) *sulphanilamido*] *aniline* (*XII*, $R = p$, $C_6H_4 \cdot NH_2$).—Red plates becoming orange yellow on pulverising, m.p. 278–82°. (Found : N, 12·6; $C_{25}H_{20}N_4O_2S$ requires N, 12·7%.)

4-[N^4-(9′-*acridyl*) *sulphanilamido*] *nitrobenzene* (*XII*, $R = p.C_6H_4 \cdot NO_2$).—Orange crystalline powder, not melting below 285°. (Found : N, 11·3; $C_{25}H_{18}N_4O_4S$ requires N, 11·9%.)

4-[N^4-(9′-*acridyl*) *sulphanilamido*] *benzenesulphonamide* (*XII*, $R = p \cdot C_6H_4SO_2NH_2$).—Orange prismatic needles, m.p. not below 280°. (Found : N, 11·0; $C_{25}H_{20}N_4O_4S_2$ requires N, 11·1%.)

The nitrogen in all these compounds was estimated by the semi-micro-Kjeldahl method of Folin. In the case of the dye and the nitro compound the products were first reduced with sodium bisulphite and then digested.

My grateful thanks are due to Lt.-Col. S. S. Sokhey, M.D., I.M.S., Director, Haffkine Institute, for his kind interest in this investigation and also to the Lady Tata Memorial Trust for the award of a Research Scholarship.

Summary

The synthesis of thirteen (N^4) amino-substituted sulphanilamide compounds of thiozal and related derivatives is described. None of them showed any activity in experimental *streptococcal* and *pneumococcal* infections in mice. Five sulphanilamide derivatives of acridine of the above group have also been described. Though some of them possessed considerable activity in the *streptococcal* infections, they were inactive in *pneumococcal* infections. It is apparent that for pronounced antibacterial action the heterocyclic ring should be substituted in the sulphonamide radical leaving a free amino group, which appears to play some significant, but as yet not perfectly understood, rôle in the mechanism of therapeutic action.

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THE GENERAL RATIONAL SOLUTION OF SOME DIOPHANTINE EQUATIONS OF THE FORM

$$\sum_{r=1}^{k+1} A_r x^{n_r} = 0$$

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1. *Introduction*

The equation

$$\sum_{r=1}^{k+1} A_r x^{n_r} = 0. \tag{I}$$

has not always non-trivial solutions, as is evident from a consideration of known results concerning Fermat's last theorem. Here and in what follows we shall mean by a solution, a rational solution. Even when non-trivial solutions exist it does not appear to be easy to obtain the general solution in some cases. For instance some solutions are known of the equation

$$x_1^4 + x_2^4 - x_3^4 - x_4^4 = 0$$

but the complete solution has not yet been found.* In this note we obtain a complete solution of (I) under the suppositions that

(*a*) $A_1 A_2 \cdot \cdot \cdot \cdot A_{k+1} x_1 x_2 \cdot \cdot \cdot \cdot \cdot x_{k+1} n_1 n_2 \cdot \cdot \cdot n_{k+1} \neq 0$,

and (*b*) *there is at least one exponent n_r which is prime to every other exponent.* Since the positive integer k is arbitrary the supposition that

$$A_1 A_2 \cdot \cdot \cdot \cdot A_{k+1} x_1 x_2 \cdot \cdot \cdot \cdot x_{k+1} \neq 0$$

involves no loss of generality. The supposition that $n_1 n_2 \cdot \cdot \cdot n_{k+1} \neq 0$ is an unnecessary restriction if there is at least one value of r for which $n_r = 1$ or -1; but if $n_r = \pm 1$ for some value of r then the problem of obtaining the general solution of (I) is obviously a trivial problem. And if

$$n_1 n_2 \cdot \cdot \cdot \cdot n_{k+1} = 0,$$

and at the same time n_r is not equal to 1 or -1 for any value of r then the supposition (*b*) cannot be realized and, it may happen that the equation (I)

* L. E. Dickson, *Introduction to the Theory of Numbers*, pp. 60–2. The complete solution of a similar equation of degree 3, *viz.*,

$$x_1^3 + x_2^3 + x_3^3 + x_4^3 = 0$$

is known. See *loc. cit.*, pp. 58–59.

has no non-trivial solution. For example the equation

$$x^2 - 1 = y^3$$

has no non-trivial solution. For, if there were such a solution, then the equation

$$X^2 + Y^3 = Z^6$$

will have the non-trivial solution $X = x$, $Y = -y$, $Z = 1$, which is impossible.‖ It may also be remarked that the result that the above equation has no non-trivial solution shows that the hypothesis, (*b*) cannot be replaced by the hypothesis that the *g.c.d* of the exponents is equal to 1. We suppose, without loss of generality, that n_{k+1} is prime to $n_1 n_2 \cdot \cdots \cdot n_k$ and that $A_{k+1} = -1$, and write the equation (I) in a somewhat more natural form thus:

$$A_1 x_1^{n_1} + A_2 x_2^{n_2} + \cdots + A_k x_k^{n_k} = x_{k+1}^{n_{k+1}} \qquad \text{(II)}$$

The principal device that I employ for obtaining the complete solution of (II) has been suggested to me by a recent paper§ of L. Tchacaloff and Christo Karanicoloff who obtain the complete solution of the equation

$$A x^m + B y^n = z^p \qquad (xyz \neq 0)$$

in the case in which m, n and p are prime to each other in pairs. The problem of obtaining the complete solution of (II) in the case in which $k = 1$ can be solved directly and easily. The complete solution of $A x^m = y^p$, where A is a rational number, $A x y \neq 0$, and $(m, p) = 1$ is given by

$$x = A^t c^p, \quad z = A^u c^m$$

where c is any rational number different from zero, and t and u are integers such that $1 + mt = up$.

2

Let $(a_1, a_2, \cdots a_t)$ denote the *g.c.d* of the t numbers $a_1, a_1, \cdots a_t$. We write

$$a_0 = (n_1, n_2, \cdots n_k) \qquad (1)$$

$$a_0 a_r = (n_1, n_2, \cdots n_{r-1}, n_{r+1}, \cdots n_k) \quad [r = 1, 2, \cdots k] \qquad (2)$$

$$L = a_0 a_1 a_2 \cdots a_k \qquad (3)$$

$$l_r = L/a_r \qquad [r = 1, 2, \cdots k] \qquad (4)$$

$$m_r = n_r/l_r \qquad [r = 1, 2, \cdots k] \qquad (5)$$

$$m_{k+1} = n_{k+1} \qquad (6)$$

$$N = m_1 m_2 \cdots m_{k+1} \qquad (7)$$

‖ B. Lind, *Archiv. Math. Phys.*, 1909, **15**, 3, 368–69. See also L. E. Dickson, *History of the Theory of Numbers*, **2**, Chap. XXVI, (paper 224), p. 766.

§ L. Tchacaloff and Christo Karanicoloff, · · · · · · *Comptes Rendus*, 1940, **210**, 281-3.

It is easy to verify that

$$(\alpha_r, \alpha_s) = 1 \qquad (r, s = 1, 2, \cdots\cdots k;\ r \neq s) \tag{8}$$

$$(m_r, m_s) = 1 \qquad (r, s = 1, 2, \cdots\cdots k+1;\ r \neq s) \tag{9}$$

$$(m_r, \alpha_r) = 1 \qquad (r = 1, 2, \cdots\cdots k) \tag{10}$$

Choose $N_1, N_2, \cdots\cdots N_{k+1}$ such that

$$N_r \equiv 0 \left(\mathrm{mod}\ \frac{N\alpha_r}{m_r}\right),\ N_r \equiv -1 \pmod{m_r} \quad [r = 1, 2, \cdots k] \tag{11}$$

$$N_{k+1} \equiv 0 \left(\mathrm{mod}\ \frac{NL}{m_{k+1}}\right),\ N_{k+1} \equiv -1 \pmod{m_{k+1}} \tag{12}$$

The choices are possible since, by (9) and (10), we have that $N\alpha_r/m_r$ is prime to m_r $(r = 1, 2, \cdots\cdots k)$, and since‡ NL/m_{k+1} is prime to m_{k+1}.

Plainly $n = 1 + N_1 + N_2 + \cdots\cdots + N_{k+1} \equiv 0 \pmod{m_r}$ $[r = 1, 2, \cdots\cdots k+1]$ and hence by (9) and (7) we see that n is a multiple of N. Let $n = aN$. Take b and c such that $b\alpha_1 + c\alpha_2 = 1 - a$. The choice is possible on account of (8). Consider the numbers $M_1, M_2 \cdots\cdots M_{k+1}$ where

$$\left.\begin{aligned} M_1 &= N_1 + b\,\alpha_1 N, \\ M_2 &= N_2 + c\,\alpha_2 N, \\ M_r &= N_r \qquad (r = 3, 4, \cdots\cdots k+1) \end{aligned}\right\} \tag{13}$$

Plainly

$$1 + M_1 + M_2 \cdots\cdots + M_{k+1} = aN + (1-a)N = N = m_1 m_2 \cdots\cdots m_{k+1} \tag{14}$$

Moreover, the numbers $M_1, M_2, \cdots\cdots M_{k+1}$ satisfy respectively the congruence equations that $N_1, N_2, \cdots\cdots N_{k+1}$ satisfy. These equations are, on account of (11), (12) and (13),

$$M_r \equiv 0 \left(\mathrm{mod}\ \frac{\alpha_r m_1 m_2 \cdots m_{k+1}}{m_r}\right) \quad [r = 1, 2, \cdots\cdots k] \tag{15}$$

$$M_r \equiv -1 \pmod{m_r} \qquad [r = 1, 2, \cdots\cdots k+1] \tag{16}$$

$$M_{k+1} \equiv 0 \pmod{\alpha_0 \alpha_1 \alpha_2 \cdots\cdots \alpha_k m_1 m_2 \cdots m_k} \tag{17}$$

Let

$$a_{ii} = 1 + M_i \qquad (i = 1, 2, \cdots k+1), \tag{18}$$

$$a_{ij} = M_j \qquad (i, j = 1, 2, \cdots k+1;\ i \neq j). \tag{19}$$

Consider the determinant Δ of order $k+1$, and of which the jth element of the ith row is a_{ij} $(i, j = 1, 2, \cdots k+1)$.

Lemma 1: $\qquad \Delta = 1 + M_1 + M_2 + \cdots + M_{k+1}$.

---

‡ Every prime divisor of NL/m_{k+1} is a divisor of $n_1 n_2 \cdots n_k$, $(n_1 n_2 \cdots\cdots n_k,\ n_{k+1}) = 1$ and $n_{k+1} = m_{k+1}$.

We have

$$\Delta = \begin{vmatrix} 1+M_1 & M_2 & M_3 & \cdots\cdots & M_k & M_{k+1} \\ M_1 & 1+M_2 & M_3 & \cdots\cdots & M_k & M_{k+1} \\ M_1 & M_2 & 1+M_3 & \cdots\cdots & M_k & M_{k+1} \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ M_1 & M_2 & M_3 & \cdots\cdots & 1+M_k & M_{k+1} \\ M_1 & M_2 & M_3 & \cdots\cdots & M_k & 1+M_{k+1} \end{vmatrix}$$

To evaluate the determinant we subtract the last row from each of the previous rows and then add to the last column every other column. Denoting by E the bottom-most element of the last column of the resulting determinant we see that

$$E = 1 + M_1 + M_2 + \cdots\cdots + M_{k+1},$$

that the other elements of the last column are equal to zero, and that the co-factor of E is a determinant each element of whose principal diagonal is equal to 1 and the rest of whose elements are equal to zero. The result of the lemma is now evident.

Let

$$b_{ij} = a_{ij}/m_i \qquad (i, j = 1, 2, \cdots\cdots k+1). \tag{20}$$

We see from (15), (16), (17), (18) and (19) that the numbers b_{ij} are integers. Let Δ' be the determinant of which the jth element of the ith row is b_{ij}.

Lemma 2. $\Delta' = 1$.

For, $$\Delta' = \Delta/m_1 m_2 \cdots\cdots m_{k+1} = 1,$$

on account of the preceding lemma and (14).

As a consequence of this lemma we have that if

$$x_i = \prod_{j=1}^{k+1} X_j^{b_{ij}} \qquad (i = 1, 2, \cdots\cdots k+1) \tag{21}$$

then

$$X_i = \prod_{j=1}^{k+1} x_j^{c_{ij}} \qquad (i = 1, 2, \cdots\cdots k+1) \tag{22}$$

where c_{ij} is the co-factor of b_{ij} in Δ'. It should be noted that the numbers c_{ij} are integers and that the set of equations (22) imply the set of equations (21).

Lemma 3.

$$c_{ii} = \pm \left(\frac{N - M_i}{N}\right) m_i \qquad (i = 1, 2, \cdots\cdots k+1),$$

$$c_{ij} = \pm \frac{M_j m_j}{N} \qquad (i, j = 1, 2, \cdots k+1;\ i \neq j).$$

The proof of this lemma is very similar to that of lemma 1, and is therefore not given here. For the purposes of this note we need the second part only of the lemma from which and from (15) we deduce that

$$c_{ij} \text{ is a multiple of } a_j \ (i, j = 1, 2, \cdots k; i \neq j) \tag{23}$$

From the lemma and from (17) we deduce that

$$c_{i\,k+1} \text{ is a multiple of } a_0\, a_1 \cdots a_k \ (i = 1, 2, \cdots k) \tag{24}$$

It is convenient to remark at this point that we see from (11), (12), (19) and (20) that

$$b_{ij} \text{ is a multiple of } a_j \quad (i, j = 1, 2, \cdots k; \quad i \neq j). \tag{25}$$

$$b_{i\,k+1} \text{ is a multiple of } a_0\, a_1 \cdots a_k \quad (i = 1, 2, \cdots k). \tag{26}$$

If now X_j be an l_j th power of a rational number for $j = 1, 2, \cdots k$, say, $X_j = a_j^{l_j}$ $(j = 1, 2, \cdots k)$, and the numbers x_i $(i = 1, 2, \cdots k+1)$ be defined by the equations (21) then we see from (3), (4), (25) and (26) that x_i is an l_i th power of a rational number for $i = 1, 2, \cdots k$. Similarly we see from (3), (4), (23) and (24) that if x_i be an l_i th power of a rational number for $i = 1, 2, \cdots k$, say, $x_i = a_i^{l_i}$ $(i = 1, 2, \cdots k)$ and the numbers X_i $(i = 1, 2, \cdots k+1)$ be defined by the equations (22) then X_i is an l_i th power of a rational number for $i = 1, 2 \cdots k$. Since the equations (21) imply and are implied by the equations (22) we can state these observations in the form of a lemma thus:

Lemma 4.—*If the integers* l_i $(i = 1, 2, \cdots k+1)$ *and* b_{ij} $(i, j = 1, 2, \cdots k+1)$ *be defined as they have been done in this note then a necessary and sufficient condition in order that the numbers* x_i $(i = 1, 2, \cdots k)$ *in the equations* (21) *be* l_i *th powers of rational numbers is that the numbers* X_i $(i = 1, 2, \cdots k)$ *are* l_i *th powers of rational numbers.*

We are now in a position to obtain the complete solution of (II). We start from the equations (21) and write them out in detail:

$$\left.\begin{aligned}
x_1 &= X_1^{\frac{1+M_1}{m_1}} X_2^{\frac{M_2}{m_1}} X_3^{\frac{M_3}{m_1}} \cdots X_{k+1}^{\frac{M_{k+1}}{m_1}} \\
x_2 &= X_1^{\frac{M_1}{m_2}} X_2^{\frac{1+M_2}{m_2}} X_3^{\frac{M_3}{m_2}} \cdots X_{k+1}^{\frac{M_{k+1}}{m_2}} \\
x_3 &= X_1^{\frac{M_1}{m_3}} X_2^{\frac{M_2}{m_3}} X_3^{\frac{1+M_3}{m_3}} \cdots X_{k+1}^{\frac{M_{k+1}}{m_3}} \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
&\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\
x_{k+1} &= X_1^{\frac{M_1}{m_{k+1}}} X_2^{\frac{M_2}{m_{k+1}}} X_3^{\frac{M_3}{m_{k+1}}} \cdots X_{k+1}^{\frac{1+M_{k+1}}{m_{k+1}}}
\end{aligned}\right\} \tag{21'}$$

If $X_1, X_2 \cdot \cdot \cdot \cdot X_{k+1}$ be such that

$$A_1 X_1 + A_2 X_2 + \cdot \cdot \cdot \cdot + A_k X_k = X_{k+1} \tag{27}$$

then a glance at the equations (21′) shows that

$$A_1 x_1^{m_1} + A_2 x_2^{m_2} + \cdot \cdot \cdot \cdot \cdot + A_k x_k^{m_k} = x_{k+1}^{m_{k+1}} \tag{III}$$

And conversely, if (III) holds and $X_1, X_2 \cdot \cdot \cdot X_{k+1}$ are the rational numbers that are defined by the equations (22) then the equations (21), which are the same as (21′), hold true, and we further get, from (21′) and (III) that (27) also is true. Hence we have proved the

Lemma 5.—A complete solution of (III) is given by the equations (21′) *where* $X_1, X_2 \cdot \cdot \cdot \cdot X_k$ *are any*¶ k *rational numbers and* $X_{k+1} = A_1 X_1 + A_2 X_2 + \cdot \cdot \cdot \cdot + A_k X_k$.

From (5), (6) and lemmas (4) and (5) we get the

THEOREM: *A complete solution of (II) is given by the equations* (21′) *where the numbers* X_i $(i = 1, 2, \cdot \cdot \cdot \cdot k)$ *are arbitrary*¶ l_i *th powers of rational numbers, and* $X_{k+1} = A_1 X_1 + A_2 X_2 + \cdot \cdot \cdot + A_k X_k$.

Summary

Recently L. Tchacaloff and Christo Karanicoloff have obtained the complete solution in rational numbers of the equation

$$A x^m + B y^n = z^p$$

in the case in which m, n and p are prime to each other in pairs. In this note the above result is generalized in two directions: The number of unknowns is taken to be any number instead of three as in the above result, and at the same time the hypothesis that the exponents are prime to each other in pairs is relaxed.

¶ $X_1, X_2, \cdot \cdot \cdot X_k$ are subject to the trivial restriction that

$$(A_1 X_1 + A_2 X_2 + \cdot \cdot \cdot \cdot + A_k X_k) X_1 X_2 \cdot \cdot \cdot \cdot X_k \neq 0$$

If $A_1, A_2, \cdot \cdot \cdot A_k$ are not rational, we should suppose further that $A_1 X_1 + A_2 X_2 + \cdot \cdot \cdot + A_k X_k$ is rational.

THE KINETICS OF THE OLEFIN-BROMINE REACTION

Part I. The Dark Reaction in Acetic Acid Solution

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The reaction between olefines and bromine has been the subject of study by several workers but the mechanism of the reaction is still far from clear. While there are numerous instances of close correlation between reactions in the gas phase and reactions in solution, we seem to have here an instance of dissimilarity. Presumably this difference can be attributed to the heterogeneity of the gas reaction as contrasted with the homogeneity of the reaction in solution.* It is recognised that the course of the reaction is governed by the polarizability of the double bond and the polarization of the bromine molecule. Substituent groups can, therefore, be expected from *a priori* considerations to affect the course of the reaction in so far as these characteristics are affected.

A theory of halogen addition with the development of integral charges on the carbon atoms was put forward by Thiele.[17] Subsequent workers† got apparently bimolecular constants for the reaction and in the competitive method adopted by Ingold and co-workers[1, 8] there is the tacit assumption that the reaction is of the first order with respect to olefin and of the same order with respect to bromine and catalysts. Preliminary investigations with crotonic and tiglic acids[2] showed that irrespective of the solvent there is a distinct induction period which varies with the nature of the olefin. The present work represents a systematic study of the reaction between bromine and monomethyl and dimethyl acrylic acids in acetic acid solution.

Whatever the exact mechanism finally adopted as correctly representing the course of the reaction, it is clear that no simple formulation will result. The reaction shows several of the characteristics of a chain reaction as may be seen by a comparison with the criteria for chain reactions enunciated by Semenoff.[15]

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* *Note.*—Some consider that the reaction in carbon tetrachloride is heterogeneous but this has still to be established. The solvent effect is under investigation by the authors.

† For a full bibliography refer Ingold and Co-workers (1 & 8) and Reference 2.

The reaction has a well-defined period of induction which varies with concentration, solvent, nature of the olefin and temperature (*vide* Tables I, II and III below, and Figs. 1 and 2).[2]

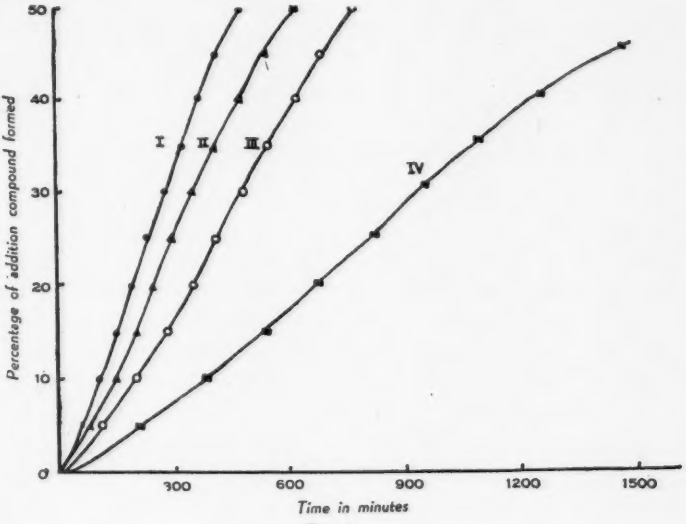


FIG. 1

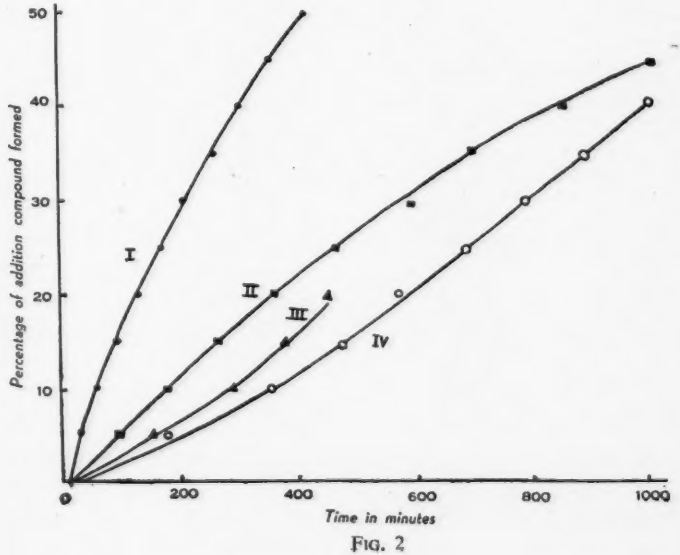


FIG. 2

TABLE I

Substance	Temperature ° C.	Solvent	Induction Period in minutes	Ref.
$CH_2=CH_2$ ..	ca 15°	CCl_4	11 min.	18
$CH_2=CH_2$ ..	ca 15°	CH_2Cl_2	4 ,,	1
Crotonic Acid ..	35·5°	Glacial Acetic Acid	25 ,,	*
	42·5		13 ,,	
	50·0		6 ,,	
Tiglic Acid ..	35·5°	,,	4 ,,	*
	42·75		2 ,,	
	49·9		1 ,,	
ββ-Dimethyl acrylic acid	35·5°	,,	1·2 ,,	*
	42·7		1 ,,	

* Present work.

TABLE II

Both Reactants same Concentration

Substance	Concentration of reactants	Induction period in minutes
Crotonic acid	M/30	25
	M/15	4
Tiglic acid	M/60	10
	M/30	4
	M/15	1
ββ-Dimethyl acrylic acid ..	M/240	16
	M/60	3
	M/30	1

TABLE III

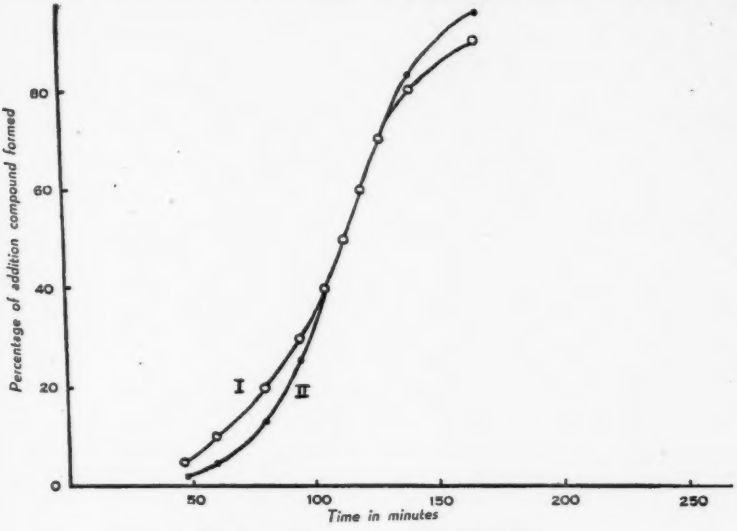
Concentrations of Both Reactants Varied Independently

Acid concentration	Bromine concentration	Induction period
Tiglic acid M/30 ..	M/60	9
Tiglic acid M/30 ..	M/120	25
Tiglic acid M/60 ..	M/120	24
Crotonic acid M/15 ..	M/30	14
Crotonic acid M/30 ..	M/15	5

An examination of the tables indicates the dominating importance of bromine concentration. This feature coupled with the known catalytic activity of hydrogen bromide[1, 2, 18] leads one naturally to the conclusion that the formation of hydrogen bromide is an important and necessary step in

the series of reactions that ultimately lead to the formation of a dibromide. At the same time, as will be indicated later on, one has to bear in mind that group influences activating the double bond may render the ' catalytic ' influence of hydrogen bromide negligible especially in a polar solvent. It is also relevant to point out here that there is no direct proportionality between the concentration of the hydrogen bromide and the velocity constant.

Besides the existence of an induction period, it is interesting to notice that the course pursued by the reaction, in the absence of a catalyst, obeys Semenoff's $e^{\phi t}$ law for reactions of the " degenerate explosion " type. Fig. 3



I. Experimental. II. Theoretical

FIG. 3

shows the experimental curve of Williams[18] and the calculated theoretical curve, using the relation

$$W_{max} = \tfrac{1}{4}(x\phi),$$

where ϕ is a parameter determined by the properties of the initial reacting mixtures. If W_{max} is expressed as the percentage reacting per second, x, the total amount reacted, becomes 100. From the slope of the curve, ϕ can be calculated. Making use of this value of ϕ and substituting in

$$x = \frac{100}{1+e^{-\phi\theta}}$$

where $\theta = t - t_{max}$ (t_{max} = time for maximum velocity) the necessary data for the theoretical curve were obtained.

In our own measurements in acetic acid solution, while an exact curve of this type is not observed, the nature of the curve approximates to that indicated by Semenoff[15] for higher concentrations. With very dilute solutions, however, even in acetic acid, the curve tends to this theoretical expectation. The deviations noticed in this connection is attributable partly to this concentration factor and partly also to the complications of a hydroxylic solvent. It has been shown by Hennion, Vogt and Weber[6] that in the reaction between ethylene and chlorine in acetic acid solution, the solvent takes part in the reaction and the same may hold good for bromine-olefin reactions too. Some of our preliminary studies indicate this as well.

It is generally accepted that the existence of a negative catalyst is characteristic of a chain mechanism and for this particular reaction antimony tribromide behaves as an inhibitor. This inhibition can arise from two causes. Either the antimony tribromide forms the pentabromide thereby diminishing the effective initial concentration of bromine or it may remove one of the products formed initially that is a necessary factor in the chain of reactions. The former alternative is not a serious difficulty since the prolongation of the induction period is out of proportion to any that can be expected from the small change in concentration. The second alternative is clearly the one in operation, since it has been found that hydrogen bromide catalyses the reaction (*loc. cit.*), the reaction is autocatalytic, with hydrogen bromide as a possible necessary link in the chain of reactions, and antimony tribromide may remove this catalyst by forming $HSbBr_4$ or H_2SbBr_5. While this postulated compound does not appear to have been described, the corresponding alkali salts are well known[10] and as such the hydrogen analogue is not unlikely.

TABLE IV

Uncatalysed, HBr Catalysed and $SbBr_3$ Inhibited Reaction

Concentration of olefin	Concentration of Br_2	Catalyst	Concentration of catalyst in mols. %	Induction period	Time for 50% reaction
M/15	M/15	None	..	4 min.	475 min.
,,	,,	HBr	1·05	0 ,,	444 ,,
,,	,,	,,	2·10	0 ,,	430 ,,
,,	,,	,,	6·90	0 ,,	260 ,,
,,	,,	ICl	0·95	0 ,,	393 ,,
,,	,,	,,	7·80	0 ,,	267 ,,
,,	,,	$SbBr_3$	1·00	20 ,,	494 ,,
,,	,,	,,	6·40	28 ,,	600 ,,

It will be shown later in the paper that the catalysed reaction gives a second order constant but though the reaction turns out to be of the first order with respect to the olefin it is not so with respect to bromine, and it is a function of hydrogen bromide concentration. Robertson *et al*[13] get third order constants falling off to second order ones at greater dilution, even this tending to smaller values in some cases. Now, reactions may be classified according to the number of reactant molecules in the stoichiometric equation or according to the number of concentrations of components, to the product of which the rate is proportional or according to the number of molecules taking part in each mechanism leading to chemical change. With a chain mechanism involving several steps one or more of these may be slow. As Fowler and Guggenheim remark[4] if there is no single step so much slower than all the others to be the rate determining step, it will usually not be possible to describe the rate by formula of the type

$$\delta v_A/\delta t = -k_n (v_A)^{n_A} (v_B)^{n_B}$$

where $n_A + n_B + \ldots = n$.

The present reaction apparently belongs to this type of complex reaction.

Further, it has been shown by Pease and Walz[12] that the thermal chlorination of methane indicated a chain mechanism similar to that of the photochemical change. It is well known that the photochemical reaction between ethylene and bromine both in the gaseous phase and in solution requires a chain mechanism and it is therefore likely that the thermal addition also depends on reaction chains, though a different mechanism may be expected with a homogeneous reaction in solution. The authors had suggested the tentative scheme (*loc. cit.*)

$$CH_2=CH_2 + Br_2 \longrightarrow CH_2=CHBr + HBr$$

$$CH_2=CH_2 + HBr \longrightarrow CH_2=CH_2$$
$$\vdots \quad \vdots$$
$$H \text{ —— } Br$$

$$HBr + Br_2 \longrightarrow HBr + Br_2^*$$

$$CH_2=CH_2 + Br_2^* \longrightarrow {}^+CH_2\text{—}CH_2Br + HBr + Br^-$$
$$\vdots \quad \vdots$$
$$H \text{—— } Br$$

$${}^+CH_2 - CH_2Br + Br^- \longrightarrow CH_2Br - CH_2Br$$

It will be noticed that this does not visualise the formation of bromine atoms. As is well known from the work of Francis[5] and of Terry and

Eichelberger,[16] addition reactions involve the polarized molecule of bromine and not atomic bromine. Also, the relative group influences necessitate initiation of addition by the positive component of this activated bromine molecule, the addition of the negative component being a relatively rapid step.

Among the compounds studied so far, all are capable of forming hydrogen bromide by substitution and in all the cases examined there is pronounced evolution of hydrogen bromide even where there is no induction period. It is clearly necessary to consider hydrogen bromide as an important link in the chain of reactions where activation of double bonds has to take place in addition to activation of the bromine molecule. This view is further confirmed when one considers the observation that with more active olefines, the minimum concentration of catalyst for eliminating the induction period becomes negligible (*cf.*, Crotonic acid and dimethyl acrylic acids). If one were to plot this minimum catalyst concentration as a function of olefin structure taking ethylene as the standard, a curve of the type (Fig. 4) may be obtained.

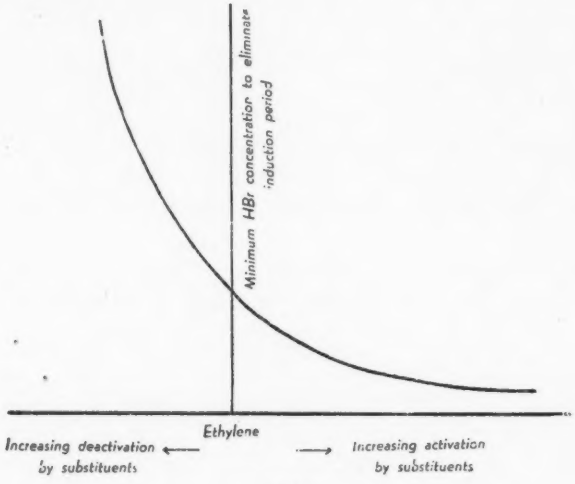

Minimum HBr concentration to eliminate induction period
Ethylene
Increasing deactivation by substituents
Increasing activation by substituents

FIG. 4

This curve can also represent the induction period as a function of group characteristic in substituted olefines in the absence of a negative catalyst, if one postulates, as we have tentatively done, that the chain mechanism must involve not only an activation of the bromine molecule but also that of the double bond.

The extreme points on the hyperbolic curve corresponding to " infinite " and " zero " concentrations of catalyst can be taken to represent respectively tetraphenyl or tetrahalogeno ethylenes and tetra alkyl ethylenes.

While it is thus seen that a chain mechanism involving hydrogen bromide is necessary, a more detailed study is needed before any correct scheme can be postulated. Further, in a study of additive reactivity of ethylene derivatives, the premises have to be examined before a comparison can be made.

Using the common equations in reaction kinetics

$$\frac{dx}{dt} = k_x\,[a-x]^1\,[\mathrm{Br}]^m\,[k_{x_1}\,(\mathrm{cat}_1)^{n_1} + k_{x_2}\,(\mathrm{cat}_2)^{n_2} + \ldots .]$$

$$\frac{dy}{dt} = k_y\,[a'-x']^{1'}\,[\mathrm{Br}]^{m'}\,(k_{y_1}\,(\mathrm{cat}_1)^{n_1'} + k_{y_2}\,(\mathrm{cat}_2)^{n_2'} + \cdots]$$

If one is to compare the relative velocities, it is necessary and sufficient that the following conditions are fulfilled:

(1) The reaction is of the first order with respect to the olefin, irrespective of the substituent groups.

(2) The reaction is of the same order with respect to the halogen, not necessarily the first.

(3) There is only one dominant catalyst and its influence is also of the same degree in all olefins taken up for comparison.

(4) The comparison is made under nearly identical conditions, there being no heterogeneous disturbances.

(5) In competitive methods, association between olefines should also be absent.*

This leads to the result

$$\frac{dy}{dx} = \frac{k_y}{k_x}\cdot\left[\frac{(a-x)^1}{(a'-x')^1}\cdot\frac{[\mathrm{Br}]^m}{[\mathrm{Br}]^{m'}}\cdot\frac{[k_{x_i}\,(\mathrm{cat}_i)^n]}{[k_{y_i}\,(\mathrm{cat}_i)^{n'}]}\right]$$

in which the factors in square brackets cancel out except for a constant on division leaving finally a ratio $\frac{k_x}{k_y}$ representing the ratio of the velocity constants.

As has been established[2] the polar solvent by itself is not a sufficient catalyst and the addition of hydrogen bromide in sufficient amount is necessary to reduce the system to an apparently simple type. The kinetics of addition of bromine to crotonic acid, tiglic acid and $\beta\beta$-dimethyl acrylic acids have been studied under these conditions (Tables V and VI).

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*C. K. Ingold (Private Communication).

TABLE V

Values of k_2 and k_3 for the reaction between trans-crotonic acid and bromine (concentration, M/15) with and without catalysts

Catalyst	(Catalyst)*		Values of k_2 and k_3 for percentage reaction						
			5%	10%	15%	20%	30%	40%	50%
..	..	$100\,k_2$	1·32	1·60	1·74	1·97	2·36	2·78	3·16
		k_3	0·81	1·02	1·14	1·33	1·72	2·22	3·79
HBr	1·05	$100\,k_2$	1·41	1·68	1·95	2·21	2·77	3·16	3·37
		k_3	0·87	1·07	1·27	1·49	2·02	2·53	4·05
,,	2·10	$100\,k_2$	1·46	1·92	2·28	2·50	2·88	3·21	3·49
		k_3	0·90	1·21	1·49	1·69	2·10	2·56	4·19
,,	6·90	$100\,k_2$	5·25	5·38	5·52	5·52	5·59	5·68	5·76
		k_3	3·24	3·41	3·60	3·72	4·07	4·55	6·92
ICl	0·95	$100\,k_2$	1·75	1·09	2·28	2·52	2·96	3·39	3·82
		k_3	1·08	1·26	1·49	1·70	2·16	2·71	4·58
,,	7·80	$100\,k_2$	3·95	5·21	5·41	5·52	5·45	5·44	5·62
		k_3	2·43	3·30	3·53	3·72	3·97	4·35	6·70
$SbBr_3$	1·00	$100\,k_2$	1·13	1·38	1·67	1·89	2·27	2·70	3·0
		k_3	0·70	0·87	1·08	1·27	1·66	2·16	3·6
,,	6·40	$100\,k_2$	0·88	1·04	1·18	1·34	1·17	1·96	..
		k_3	0·54	0·66	0·77	0·90	1·21	1·57	..

* Molar percentage of catalyst per mol. of each reactant.

TABLE VI

Comparison of values of k_2 for the addition of bromine to trans-crotonic, tiglic and ββ-dimethyl acrylic acids (concentration of reactants, M/30)

Acid	Temperature °C.	Values of $100\,k_2$ for percentage reaction						
		5%	10%	15%	20%	25%	30%	40%
trans-Crotonic ..	35·5	0·72	0·88	0·99	1·11	1·22	1·35	1·57
Tiglic	35·45	5·85	6·95	7·67	8·28	8·85	9·47	10·61
ββ-Dimethylacrylic	35·5	39·9	49·4	54·0	57·5	59·9	61·2	61·0

An examination of the tables shows that under controlled catalytic conditions, the reaction gives a "bimolecular" constant which varies with the nature of the olefin. In our hands, this addition reaction fails to give the termolecular constants reported by Robertson for cinnamic acid.

Confining our attention just now to the bimolecular constants, a systematic variation of the different reactants resulted in the conclusion that the reaction is of the first order with respect to the olefin.

TABLE VII

Effect of concentration of crotonic acid on the rate of addition of bromine to crotonic acid, catalysed by hydrogen bromide ($t = 35{\cdot}5°$ C.)

Solution			Time (mins.) taken for percentage reaction						
(Acid)	(Br_2)	(HBr)	5%	10%	15%	20%	25%	30%	40%
M/10	M/30	11·01%	16	33	51	70	91	113	163
M/15	,,	,,	25	51	80	110	142	176	256
M/20	,,	,,	30	65	102	141	185	233	345
M/30	,,	,,	45	101	160	224	294	374	..

TABLE VIII

Effect of concentration of tiglic acid on the rate of addition of bromine to tiglic acid, catalysed by hydrogen bromide ($t = 35{\cdot}5°$ C.)

Solution			Time (mins.) taken for percentage reaction							
(Acid)	(Br_2)	(HBr)	5%	10%	15%	20%	25%	30%	40%	50%
M/10	M/30	11·01%	3	6·1	9·4	12·7	16·8	21·0	32·2	46·2
M/15	,,	,,	4	8·9	14·0	19·2	25·5	32·2	49·4	72·8
M/20	,,	,,	5·2	11·4	18·2	25·6	34	44·6	69·3	100·8
M/30	,,	,,	8·6	18·2	29·0	42·2	55·8	71·5	112·5	..

As an approximation, it is well known that in reactions of the first order, the time required for the same extent of the reaction (expressed in mols. per cent.), is inversely proportional to the concentration. Bearing in mind that all the reactants are present in comparable amounts, it will be noticed that this relationship holds good as regards the unsaturated compound, when

the concentration of bromine and of hydrogen bromide is kept constant, while olefin concentration was varied (*vide* Tables VII and VIII above).

A similar process of " isolation " applied to bromine and to hydrogen bromide, however, leads to different results. Whatever the " order " of the reaction may be, it is clearly not of the " first order " in either case.

TABLE IX

Effect of concentration of bromine on the rate of its addition to trans-crotonic acid, catalysed by hydrogen bromide ($t = 35 \cdot 5°$ C.)

Solution			Time (mins.) taken for percentage reaction							
(Acid)	(Br_2)	(HBr)*	5%	10%	15%	20%	25%	30%	40%	50%
M/15	M/30	11·01	26	55	85	120	157	195	282	384
,,	2M/75	,,	22	45	72	102	133	166	232	312
,,	M/50	,,	19	41	65	90	115	141	193	245
,,	M/75	,,	23	45	66	87	109	131	178	230
,,	M/150	,,	22	43	66	94	122	153	232	347

*Concentration is expressed as molar percent. per mol. of olefin.

TABLE X

Effect of concentration of bromine on the rate of its addition to tiglic acid, catalysed by hydrogen bromide ($t = 35 \cdot 45°$ C.)

Solution			Time (mins.) taken for percentage reaction							
(Acid)	(Br_2)	(HBr)*	5%	10%	15%	20%	25%	30%	40%	50%
M/15	M/30	5·51	4·4	8·8	13·5	19·0	25·0	31·9	48·9	71·2
,,	2M/75	,,	4·8	10·0	15·7	21·8	28·9	36·9	56·8	84·5
,,	M/50	,,	5·8	12·0	18·8	26·3	35·1	44·8	67·7	98·0
,,	M/75	,,	7·6	15·5	24·4	34·0	45·0	57·4	88·5	..
,,	M/150	,,	10	20·8	32·0	45·6	63·3	86·4	..	..

*Concentration is expressed as molar percentage per mol. of olefin.

TABLE XI

Effect of concentration of bromine on the rate of its addition to ββ-dimethylacrylic acid, catalysed by hydrogen bromide ($t = 35 \cdot 5°$ C.)

Solution			Time (mins.) taken for percentage reaction							
(Acid)	(Br_2)	(HBr)*	5%	10%	15%	20%	25%	30%	40%	50%
M/30	M/60	11·01	3·8	8·1	12·5	17·6	23·1	29·4	45·7	68·2
,,	M/75	,,	4·7	9·4	14·4	20·2	26·6	34·0	52·1	75·5
,,	M/100	,,	5·7	11·6	17·6	24·6	32·3	41·0	62·2	90·4
,,	M/150	,,	7·0	14·2	22·4	31·6	42·0	53·0	79·2	114·0
,,	M/300	,,	11·8	23·6	36·4	50·8	67·5	85·0	125·8	..

*Concentration is expressed as molar percentage per mol. of olefin.

TABLE XII

Effect of concentration of hydrogen bromide on the rate of addition of bromine to trans-crotonic acid, (concentration of reactants, M/30) ($t = 35 \cdot 5°$ C.)

Mols. % of HBr	Time (mins.) taken for percentage reaction						
	5%	10%	15%	20%	25%	30%	40%
44·04	17	35	57	80	107	138	219
22·02	26	53	87	120	162	210	331
11·01	45	101	160	224	294	374	..
5·51	69	145	228	315	412	522	782
2·76	105	213	322	438	567	702	1015
1·38	134	270	402	532	670	805	1132
0·00	218	380	535	675	822	955	1275

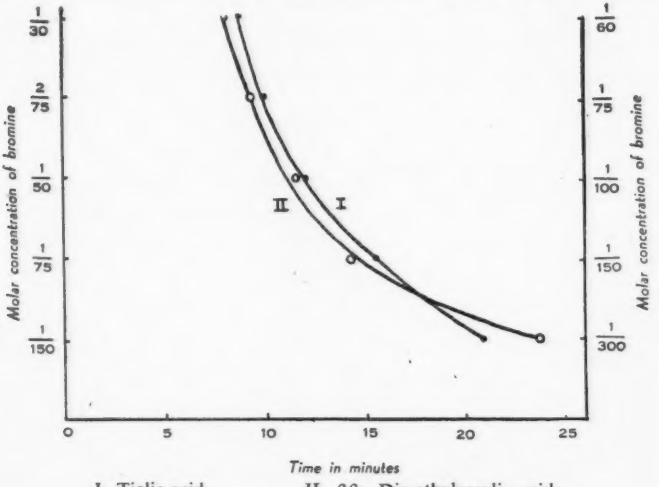
TABLE XIII

Effect of concentration of hydrogen bromide on the rate of addition of bromine to tiglic acid (concentration of reactants, M/30) ($t = 35 \cdot 5°$ C.)

Mols. % of HBr	Time (mins.) taken for percentage reaction							
	5%	10%	15%	20%	25%	30%	40%	50%
44·04	4·2	9·0	14·5	20·5	28·0	36·4	61·3	99·5
22·02	5·8	12·0	19·2	28·0	37·7	49·5	81·8	131·0
11·01	8·6	18·2	29·0	42·2	55·8	71·5	112·5	..
5·51	12·0	25·6	40·0	55·0	72·7	93·5	145·0	221·5
2·75	16·3	33·2	50·0	68·5	88·5	110·8	167·5	249
1·38	19·5	38·2	57·0	76·5	97·5	120·5	177·5	263·0
0·00*	27·0	48·0	69·0	90·6	113·0	135·7	188·4	..

* This reaction alone was carried out at 35·45° C.

Comparing the time taken for the same extent of reaction (10% has been chosen for the curves) the general nature of the curve (Fig. 5) indicates that



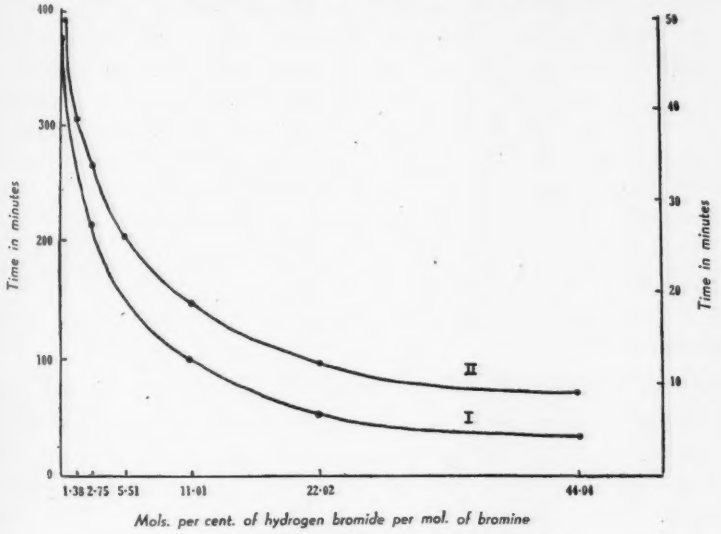
I. Tiglic acid. II. $\beta\beta$—Dimethylacrylic acid.

FIG. 5

the order of the reaction is the same with respect to bromine in this addition process. When both olefin and hydrobromic acid are present in excess,

crotonic acid, however, presents an anomalous case in concentrations of the order of M/75 as the reaction then appears to be independent of bromine concentration.

With hydrogen bromide as the variant (Fig. 6) there is no direct proportionality between concentration of catalyst and time taken for the same



I. *tran*—*Crotonic acid.* II. Tiglic acid.

FIG. 6

extent of the reaction. Hydrogen bromide in this reaction falls in the category of catalysts showing considerable and specific variations when present in small quantities but tending to a maximum of activity at higher concentrations. In a reaction in which molecules can acquire slowly the energy of activation in the absence of a catalyst while the catalyst speeds up the process, it can be shown that the reaction should be of the first order with respect to the reactant and for various catalysts the maximum should be the same.[7] Again, if, while molecules are activated independently, the co-operation of the catalyst is needed for final transformation, the reaction should be of the second order and the limiting rate independent of the nature of the catalyst. On the other hand, if reactant molecules are activated by the catalyst and the two remain temporarily associated in the form of a complex that undergoes the completed reaction, at the same time exposed to deactivation by further collisions, the reaction should be of the first order with respect to the reactant and the limiting value will vary with catalyst.

An examination of tables given before suggest that such a complex is likely in the present case.

Experimental

The reactions were carried out in an electrically heated thermostat of the usual type, care being taken to shut out all access of light inside the vessel. The temperatures were maintained within the range $\pm 0{\cdot}015°$ C. Pure benzene, crystallisable, for molecular weight determinations, was shaken with mercury for several days before use in the thermoregulator. The choice of benzene rather than toluene the usual liquid used in thermoregulators was determined by its greater expansion and ease of purification. The reactants were kept in dark amber-coloured, glass-stoppered bottles and the course of the reaction followed by iodimetric estimation of the halogen. Amber coloured pipettes, further darkened in the bulb portion, were used in transferring solutions. The number of readings and the volume taken for each reading were determined by statistical considerations for accuracy.

A. R. acetic acid was used after purification by the method of Orton and Bradfield.[11]

Bromine was purified by the method of Anantakrishnan and Ingold.[1]

Hydrogen bromide was prepared by the action of bromine on decalin the resulting gas being purified by passing through a train consisting of U-tube cooled to $-78°$ with solid carbon dioxide and methanol, a tower of naphthalene, two tubes of phosphorous pentoxide and a tower of glass wool, before absorption in purified acetic acid. The hydrogen bromide content of this solution was estimated before each experiment. Kahlbaum's pure iodine monochloride and antimony tribromide were used after distillation, rejecting head and tail fractions.

Crotonic acid was prepared by the method of Scheibler and Magasanik.[14]

Tiglic Acid.—The B. D. H. product was used after recrystallisation to constant melting point.

ββ-Dimethyl Acrylic Acid.—The method described by Sikhibhushan Dutt[3] failed to give any yield of the acid in our hands. A modified method of Massot[9] was therefore adopted. A mixture of malonic acid (1 mol.), acetic anhydride (1·2 mols.) and dry acetone (4 mols.) was refluxed on the water-bath for three days. The brownish green fluorescent solution was distilled under ordinary pressure, fractions upto 130° C. being collected to remove excess acetone and acetic acid. The residue was then distilled under reduced pressure. The remaining acetic acid distilled at 56°/40 mm., the ββ-dimethyl acrylic acid distilling at 112°/20 mm. (yield 25% theoretical). The reduced

yield is probably due to formation of dimethyl glutaric acid as by-product. Distillation under ordinary pressure was not satisfactory, since the boiling point 195°–200° was very near the decomposition point (204°).

Summary

The kinetics of the olefin-bromine reaction has been studied in acetic acid solution using three related aliphatic monobasic acids. The course of the reaction clearly indicates a chain mechanism. It is found that the reaction is of the first order with respect to the olefin and the influence of the catalyst hydrogen bromide is pronounced, the experimental evidence favouring a complex formation between olefin and catalyst.

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THE KINETICS OF THE OLEFIN-BROMINE REACTION

Part II. The Critical Increment of the Reaction in Acetic Acid

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It has been shown in Part I that this reaction requires a chain mechanism and that in the presence of a dominant catalyst, an apparently bimolecular constant is obtained. In this part will be presented the influence of temperature on the reaction.

It has already been shown that even in the uncatalysed, autocatalytic reaction, temperature exerts a profound influence, the induction period being completely eliminated at higher temperatures in some cases. The consequences of this thermal activation is felt to an even greater extent in the catalysed reaction. The results are summarised in Tables I, II, III and IV.

Table I

Effect of temperature on the hydrogen bromide catalysed reaction between bromine and trans-*crotonic acid*

Concentration of reactants	Concentration of Hydrogen Bromide (mols. %)	Temperature °C.	Time (mins.) taken for percentage reaction					$100\,k_2$ for 20% reaction	E (calories)
			10%	20%	25%	30%	40%		
M/30	11·01	49·95	36·8	88·0	117·2	148·6	226	8·523	10,140
,,	,,	42·50	57·2	128·0	170·0	218·4	344	5·860	11,840
,,	,,	35·40	92·6	198·0	260·6	337	..	3·787	9,790
,,	,,	25·15	157·2	339	460	..	..	2·213	
M/15	,,	49·95	10·8	24·8	32·8	42·2	65	15·12	10,400
,,	,,	42·50	16·3	36·4	48	61·2	94	10·30	9,840
,,	,,	35·40	24·2	52·3	69·4	90·0	142	7·169	8,840
,,	,,	25·15	39·2	86	114·8	147·8	238	4·360	

TABLE II

Effect of temperature on the hydrogen bromide catalysed reaction between bromine and tiglic acid

Concentration of reactants	Concentration of Hydrogen Bromide (mols. %)	Temperature ° C.	Time (mins.) taken for percentage reaction					100 k_2 for 20% reaction	E (calories)
			10%	20%	25%	30%	40%		
M/30	11·01	50·05	11	23·8	31·4	41	66	31·52	6,670
,,	,,	42·25	13·5	30·8	40·7	52·4	86	24·35	5,690
,,	,,	35·50	16	37·6	50·3	65·4	105·8	19·95	6,160
,,	,,	30·10	20·0	45	60·8	78·2	126·4	16·66	
M/15	,,	50·05	2·18	4·75	6·37	8·35	12·7	78·94	6,210
,,	,,	42·25	2·64	6·04	8·04	10 62	17·3	62·09	6,180
,,	,,	35·50	3·25	7·50	10·14	13·12	21·1	49·99	7,520
,,	,,	30·20	4·25	9·34	12·35	16·06	26·0	40·15	

TABLE III

Effect of temperature on the hydrogen bromide catalysed reaction between bromine and ββ-dimethyl acrylic acid

Concentration of reactants	Concentration of Hydrogen Bromide (mols.%)	Temperature ° C.	Time (mins.) taken for percentage reaction					100 k_2 for 20% reaction	E (calories)
			10%	20%	25%	30%	40%		
M/60	11·01	50·3	13	28	37·3	48	76·2	53·57	6·370
,,	,,	42·6	15·6	35·7	47·8	61·5	97·4	42·02	5,800
,,	,,	35·5	20·4	44·2	58·3	75·3	119·6	33·94	6,920
,,		31·6	22·8	50·4	67·6	88·3	150	29·77	
M/30	,,	50·3	3·20	6·92	9·18	11·90	19·1	108·4	4,400
,,	,,	42·6	3·72	8·18	10·92	14·4	23·2	91·68	4,460
,,	,,	35·5	4·24	9·64	12·94	16·88	27·4	77·80	

TABLE IV

Comparison of values of k_2 for the reaction between bromine and trans-*crotonic tiglic and ββ-dimethyl acrylic acids, catalysed by hydrogen bromide (concentration of reactants, M/30) (HBr) = 11·01*

Acid	Temperature °C.	100 k_2 for 20% reaction	E (calories)
trans-Crotonic ..	35·4	3·79	10,100
Tiglic	35·5	19·95	6,400
ββ-Dimethyl acrylic	35·5	77·80	4,400

Hinshelwood and co-workers[2] have shown in other organic reactions the structural influences on energy of activation and it is interesting to examine the relationship in the present instances. At the outset it must be pointed out that quantitative conclusions cannot be drawn at the present stage, but the significant fact will be noticed that substitution of hydrogen by a group belonging to class I of Ingold's classification[3] leads to a lower energy of activation for the addition reaction. The experimental values using the Arrhenius equation $k = Ae^{-E/RT}$ are surprisingly low when one compares them with the theoretical deductions of Sherman and co-workers[4] using the " transition-state " method for the ethylene-bromine reaction. This wide divergence is attributable to several factors: (i) substituted ethylenes may not be expected to require the same energy of activation as the simple unsubstituted ethylene. Before any generalization as to group influences on energy of activation can be made, a better knowledge of mutual group interactions is necessary than is available at present. From *a priori* considerations, however, it can be deduced that the presence of groups activating the ethenoid linkage will tend to lower the energy of activation for the addition reaction as is seen to be the case.

(ii) The " transition-state " method, while it has proved successful in the simpler bimolecular reactions, has still to be applied with success to chain reactions. Treatment of the system as a simple four-electron problem can at best be only a crude approximation.

(iii) The intervention of the solvent cannot be totally excluded, especially, when a polar, hydroxylic solvent is involved as in the present case. It is implicit in the direct calculation of E that there is no great variation in the probability factor. One must admit, however, that the more accurate computation of E will be from the slope of the Log K – 1/T curve (Fig. 1).

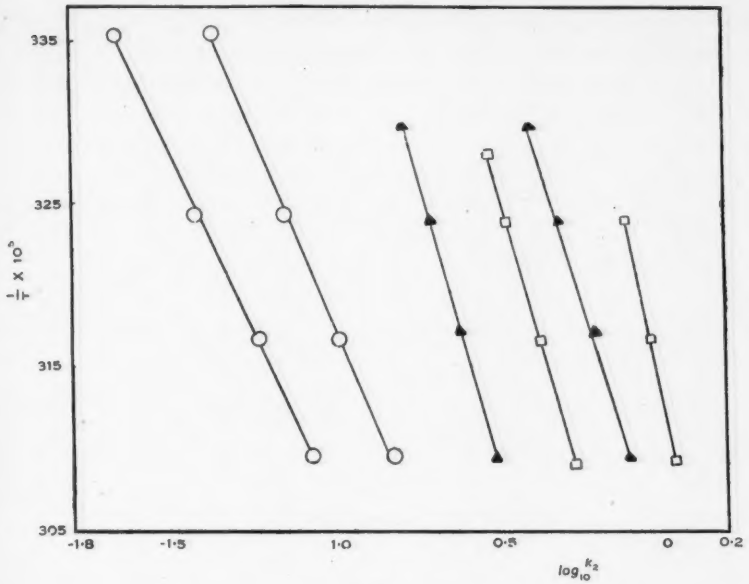

FIG. 1

O-Crotonic acid; ▲-Tiglic acid; □-Dimethyl acrylic acid.

Concentration of reactants: I. M/30. II. M/15 for crotonic and tiglic acids. Dimethyl-acrylic acid: I. M/60. II. M/30.

While the introduction of a second methyl group definitely lowers the energy of activation, the value of E appears to be independent of the relative position of the activating groups with reference to the ethenoid link. The observed difference in reaction velocity between tiglic acid and $\beta\beta$-dimethyl acrylic acid is obviously due to a difference in the probability factor. No doubt, the greater reactivity of the compound with asymmetric methyl groups can be anticipated from considerations of electromeric displacements as well as of dipole moment. There are, however, limitations to the conclusions that can be drawn from these. While there is a certain amount of correspondence between increased dipole moment and activity of the double bond, it has been noticed that an increase in the number of activating groups results in increased activity even where the moments oppose each other (*cf.*, asym. dimethyl ethylene and tetramethyl ethylene). With the same substituents the compound with a higher dipole moment may be expected to be more reactive, *i.e.*, asymmetric substitution may have a dominant influence. In comparing a series of alkyl ethylenes, this phenomenon was encountered and it was then anticipated[1] that symmetrical dimethylethylene

should react at a slower rate with bromine than the asymmetrical analogue. In the present instance we have the analogous position except for the complication of a carboxyl group that will affect the quantitative aspect of the addition (Table V).

TABLE V

Substance	Substituted product		Relative increase in speed of addition
$CH_3CH = CH_2$	Symmetrical	Butene-2	2·2*
	Asymmetric	2 methyl propene-1	3·5**
$CH_3CH = CH\ COOH$	Substituent in 2 position	Tiglic acid	5**
	Substituentin 3 position	Dimethyl acrylic acid	19**

* Calculatd value ** Experimental values

It is necessary, here, to consider the relative values of E and of PZ in this case in greater detail. Using molecular models of the type designed by H. A. Stuart[5] the mean molecular diameters are as given in Table VI.

TABLE VI

Substance	Mean mol. diameter in A $\times 10^8$
trans-Crotonic acid ..	6·8
Tiglic acid ..	7·5
$\beta\beta$-Dimethyl acrylic acid ..	7·5

It will be noticed that the molecular dimensions of the two dimethyl acrylic acids ($\alpha\beta$ and $\beta\beta$) are approximately the same and as such no great difference in the collision number may be expected. This naturally means that the greater reactivity of the $\beta\beta$ acid is attributable to an orientation effect. This cannot, however, explain the variation in E with concentration. The tendency to rise with increasing dilution suggests that in the limiting case of the unsubstituted olefin, the value calculated by Sherman may be obtained, especially if a nonpolar solvent is used. This investigation is now in progress.

It is thus clear that much more information than is available now is needed before any theoretical treatment with rigorous methods can be developed to explain all the vagaries of this apparently simple reaction. We are, however, justified in concluding that the ethylene-bromine reaction involves the activation of the bromine molecule as well as the activation of the double bond. Where structural influences are insufficient for such activation the role of the catalyst becomes an important factor, such catalytic activation presumably diminishing with increase of temperature. The change in the energy of activation with concentration and the necessity for the introduction of an orientation factor require an approach from the " transition-state " method for any calculation of reaction constants.

Experimental

The procedure adopted is the same as in Part I, a more steady temperature being obtained with a surface-layer of liquid paraffin for higher temperatures. The nature of the solvent precluded measurements beyond the ranges investigated.

Summary

The dark reaction, catalysed and uncatalysed, between methyl substituted acrylic acids and bromine has been investigated at 25° C., 35° C., 42° C., ard 50° C. in glacial acetic acid solution. An analysis of the critical increment shows not only group influence but also an orientation effect.

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RAMAN SPECTRA AND HYDROXYL FREQUENCIES OF SOME FATTY ACIDS

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1. Introduction

Martin and collaborators (1936) have stated that in strong electrolytes like sulphuric and trichloracetic acids the frequency corresponding to the O–H band, is not observed and therefore, these acids are completely ionised even in the pure state. Further Hibben (1939) reports that there is no indication of any O–H frequency in anhydrous or even 50% acetic acid. Venkateswaran (1938) was able to show the presence of an O–H frequency in sulphuric and other strong inorganic acids. The study of the fatty acids especially trichloracetic acid was therefore undertaken to find the presence of an O–H frequency in them. It was also considered desirable to study the spectra of trichloracetic acid in various states (solid, liquid and aqueous solutions), because a detailed study had not been made previously.

2. Experimental

The acids investigated in this paper are hygroscopic, and so the traces of water present were removed by distilling them twice at sufficiently low pressure before sealing off the experimental tube. A filter of iodine in CCl_4 was used to cut off the 4358 excitation, and in some cases, a filter of sodium nitrite was also used as complementary filter.

3. Results

The results are given in the following tables:

TABLE I

Trichloracetic Acid

Kohlrausch	Peyches	Author				Remarks
Molten	Solution	Solid	Molten	25% Water solution	75% Water solution	
		3597 3171				Very weak band
		3150 (1) 2996 (1) 2852 (1)				A weak band showing a triplet structure, the centre being at 2996
		2627 (1)				
1743 ($\frac{1}{2}$)	1743 (*f*)			1750 ($\frac{1}{2}$)	1750 (3)	
1689 (0)	1641 (*f*)				1641 (3) *br*	Water band
1413 ($\frac{1}{2}$)		1434 (3)	1435 ($\frac{1}{2}$)		1433 (0)	
					1370 (0)	
	1332 (*m*)		1330 ($\frac{1}{2}$)	1332 (1)	1332 (4)	Becomes stronger at high dilutions
		1260 (2)				
946 (3)	951 (*m*)	956 (2)	952 (1)	952 (1) *s*	952 (4)	
833 (5)	839 (F)	842 (0)?	842 ($\frac{1}{2}$)	836 (4)	836 (8)	Gains in sharpness on dilution
		833 (4)	833 (2)			
					735 (1)	
				695 (1)	695 (1)	
676 (6)	678 (F)	675 (8) *s*	675 (4)	675 (2)	675 (1) (W. diff.)	Strong and sharp in solid, weak in liquid and becomes more and more diffuse on dilution
		511 (1)				
447 (10)		455 (4)	450* (10)	Absent	Absent	
433 (10)	432 T F	..	433 (10)	433 (15)	433 (20)	Gains very much in intensity on dilution
318 (3)			320 (2)			
277 (10)	281 T F		282* (10)	282* (10)	282* (12)	
200 (10)	192 F		202* (10)	202 (10)	202 (10)	
			102* (3)			Vanishes on dilution

* These lines have fairly strong anti-stokes components.

TABLE II

Formic Acid—Acetic Acid— Dichloracetic Acid

Formic Acid		Acetic Acid		Dichloracetic Acid	
Raman Frequencies	Polarisation	Raman Frequencies	Polarisation	Raman Frequencies	
3466–2962 (Weak diffuse band)		3466–2932 (Weak diffuse band)		3530–3038	(Very weak diffuse band)
				2938–2400	(,,)
2962 (8)	P	3027 (5) *s*	D	3035 (10)	
2778 (2)	P	2982 (5) *s*	D	3020 (0)	
2592 (0)	..	2934 (20)	P	1445 (3)	(Broad and diffuse with a sharp edge at 1445)
2130 (0)	..	†2849 (3)	..	†1421 (3)	
		†2680 (0)	..	†1302 (0)	
1730 (2)	D	†2627 (0)	..	1248 (0)	
1672 (4)	P	†2580 (0)	..	1210 (3)	
1398 (10)	P	1720 (0)	D	925 (5)	
1350 (0)	P	1669 (2)	P	821 (8)	
1197 (2) *br*	P	1435 (5) *v.br*	D	774 (7)	
1057 (2)	D	1363 (3)	P	675 (10)	
865 (1)	P	1270 (1)	D	445 (2)	
698 (0)	D	1120 (0)	?	419 (8) *s*	
675 (3)	D	1020 (1)	P		
189 ± 80 (3)	D	895 (15)	P		
		† 882 (2)	P		
		725 (0)			
		620 (6)	D		
		600 (2)	D		
		452 (4)	D		

†New frequencies observed by the author.

TABLE III

O–H Frequencies in Fatty Acids

	Band Width			Shift from the normal (O–H) frequency in KOH, *viz.*, 3608
	Beginning	Middle	End	
Formic Acid ..	2962	3210	3466	398
Acetic Acid ..	2932	3200	3466	408
Dichloracetic Acid	3038	3284	3530	324
	2400	2668	2938	Very weak band
Trichloracetic Acid ..	3597	3384	3171	,,
	3150	2996	2852	612

Trichloracetic Acid.—This acid has been investigated by a number of workers namely Thatte (1936, molten), Peyches (1935, solution), Kohlrausch and Pongratz (1933, molten), Ghosh and Kar (1931, solution), Woodward (1931, solution) and Bernstein (1936, solution). Of these the more thorough investigations are those of Peyches for solution and of Kohlrausch for the molten substance, and these are included in Table I. Others have recorded only a few lines and their results are not stated here. The author's results are in good agreement with the results of these workers, and also show some new frequencies in solution. The O–H band is very weak and so a long exposure with a wide slit is necessary to bring it out. It is noticed that the solid and liquid are fluorescent whereas the spectrum of the same sample in solution is free from fluorescence.

Dichloracetic Acid.—The substance has been investigated by Woodward, Thatte and Kohlrausch. The author's results though incomplete in the low frequency region show some new results. The frequency 1435 which is a very broad band in acetic acid has split into two frequencies and the C–H frequency at 3035 is accompanied by a faint diffuse line. The O–H band in dichloracetic acid is very weak.

Acetic Acid.—The number of investigations on this substance is quite large (see Hibben's bibliography for references). The picture reproduced here shows several new frequencies. The frequency 882 which is a close companion to the strong line 895, the C–H frequencies 2849, 2680, 2627 and 2580 and the O–H band have been observed for the first time. Frequencies reported by Kohlrausch (1933) for acetic acid are 445 (2), 621 (5), 893 (9), 1275 ($\frac{1}{2}$), 1363 ($\frac{1}{2}$), 1429 (256), 1663 ± 7, 2937 (12), 2986 (1), and 3033 (11).

4. *Discussion*

1. *Trichloracetic Acid.*—The results of the investigation may be stated as follows: (1) The frequency 102 vanishes in solution. (2) The line 450 is present in solid and liquid but is absent in solution whereas the line 433 is present in the liquid and solution but is absent in the solid. (3) The frequency 676 is very sharp and the strongest line in the solid, but becomes weak in the liquid, and more diffuse in solution. New lines 695 and 735 develop

with increased dilution. (4) The frequency 833 is diffuse in the solid, appears diffuse and accompanied by a faint companion in the liquid, and becomes sharp on increased dilution. (5) The line 1332 is not present in the solid, very weak in the liquid, and is fairly strong in solution. (6) The frequency 1434 is strong in solid but very weak in the liquid and solution. (7) The frequency 1750 appears fairly strong in solution although their presence in the liquid is not easily detectable. These results are similar to those observed by several workers in inorganic acids, in which certain lines fall off in intensity as the acid is diluted and these are assigned to the undissociated molecule. Lines not present in the pure acid but appearing and becoming stronger on dilution are attributed to ions, and the lines which remain unchanged on dilution appear to belong to ions as well as molecules. On the basis of this classification, the lines 1434, 676, 450 and 102 are characteristic of the undissociated molecule and the lines 1758, 1322, 833, 735, 695 and 433 are characteristic of the monomer and the ion. The frequencies 202, 284 and 952, belong to both ions and undissociated molecules. The process of dissociation consists of two parts, (1) the breaking up of polymers into single molecules and (2) the breaking up of monomers into ions. In the initial stages of dilution, the changes will be mostly due to the first process. Therefore, it appears reasonable to conclude that the frequencies 1434, 675, 450 and 102 which are strong in the solid and in the liquid (excepting 1434) and become very weak or completely vanish on dilution, are due to the associated molecules. The frequencies 1758, 1332, 833 and 433 which are increased in intensity on dilution are due to monomer while the frequencies 695 and 735 which appear only on dilution are due to the ions. According to Edsall (1936), in fatty acids which are associated, the carbonyl frequency is considerably lowered and appears at 1650. The existence of the normal carbonyl frequency at about 1720 in these acids would thus indicate the presence of monomers. Recently Sunanda Bai (1940) has confirmed these assignments by showing that isobutyric acid has only one $C=O$ frequency at 1650 at room temperature, but when the temperature is raised to the boiling point a new diffuse line appears at 1710 indicating that the monomer is formed in appreciable numbers. The presence of a weak line at 1743 in the liquid (Kohlrausch) indicates that in the molten condition there is a partial depolymerisation of the acid.

The progressive transition of the molecule from the associated to the ionic condition is well illustrated by the continuous weakening and the increasing diffuseness of the line 675 as we pass from the solid to the solution and also by the increasing sharpness of the line 833 which is diffuse and broad in the solid and the liquid. The position of the hydroxyl frequency

in the region 3150–2852 also supports the above conclusion because the greater the shift is for the hydroxyl frequency from the normal value, the weaker is the O–H binding and therefore the stronger is the association. The effect of monomeric and polymeric association in the infra red has been investigated by a number of workers, namely, Errera and Mollet (1937), Fox and Martin (1937), Freymann (1937), Badger and Bauer (1937) and they report that the monomeric form of the molecule gives sharp bands corresponding to the fundamental frequencies while the polymeric form gives broad bands which are very weak. Davies and Sutherland (1938) report an association band in trichloracetic acid which extends from $2{\cdot}9\mu$ to $3{\cdot}3\mu$, that is from 3450 to 3030 cm.$^{-1}$ while the monomeric absorption occurs at 3500. It is probable that the weak band extending from 2852–3150 observed in the Raman effect corresponds to the band 3450–3030 in the infra red and is characteristic of the polymeric association, as has been suggested by Venkateswaran (1938) for inorganic acids. Cheng and Le Compte (1936) have reported the frequencies 1210, 947, 835, 700 and 671 for the infra red spectrum of trichloracetic acid in the molten condition. The lines 947, 835 and 671 coincide with those observed in the Raman spectrum and are, therefore, the fundamental frequencies of the molecule. Of the frequencies of the ion, $\left[\text{C–C}\begin{matrix}\nearrow\text{O}\\\searrow\text{O}\end{matrix}\right]$, *viz.*, 1752, 1332, 833, and 433, 1752 represents the antisymmetric oscillation and 1332 the symmetric oscillation of the carboxyl group $\left[\text{C}\begin{matrix}\nearrow\text{O}\\\searrow\text{O}\end{matrix}\right]$, and 833 the C–C valence frequency and 433 the C–C$\begin{matrix}\diagup\text{O}\\\diagdown\end{matrix}$ deformation frequency.

Formic Acid.—The number of lines observed in formic acid is far more than can be explained on the basis of the simple chemical formula HCOOH. The molecules therefore exist as dimers or higher polymers. From the electron diffraction studies of Pauling and Brockway (1934) it is known that the molecules exist as dimers even in the vapour state. We may therefore assign the strong polarised lines 2962, 2778, 1672, 1398, 1197 and 865 and the two strong depolarised lines 1057 and 675 to the polymer. There are, however, some weak Raman lines 1730, 1350 and 698 accompanying the strong lines at 1672, 1398 and 675 which may be assigned to the monomer form of the molecule. It is interesting to note that the carbonyl frequencies 1672 and 1730 in formic acid show a different behaviour, the former being polarised and the latter depolarised. This behaviour suggests that the frequency 1730 represents monomer molecules because a valence asymmetric

vibration of the carboxyl $\left[C\begin{smallmatrix} O \\ \diagdown \\ \diagup \\ O \end{smallmatrix} \right]$ in the monomer will be depolarised while the same oscillation in a dimer molecule will be polarised as the latter possesses a centre of symmetry. Bonner and Hofstädter (1938) report the following lines for the monomer in the infra red: 3570, 2940, 1740, 1093 and 658. We may, therefore, reasonably consider the lines 2940, 1740, 1350 and 1093 as the planar frequencies of the monomer molecule $\left[H\text{–}C\begin{smallmatrix} O \\ \diagdown \\ \diagup \\ O \end{smallmatrix} \right]$ and the line 698 as the perpendicular frequency. 1350 is the symmetric oscillation and 1740 the antisymmetric oscillation of the carboxyl group. The above assignment of 1350 agrees with that of Edsall (1936). The force constants in the molecule can now be evaluated by solving the secular equation for the molecule $H\text{–}C\begin{smallmatrix} O \\ \diagup\!\!\diagup \\ \diagdown \\ (OH) \end{smallmatrix}$. The secular equation is of the fifth degree, but a simplification is obtained as the mass of hydrogen is small. We find that the k (C–H) force constant is $5{\cdot}14 \times 10^5$ dynes. Using the (C–O) force constant $= 5{\cdot}0 \times 10^5$ dynes, (C = O) force constant as $9{\cdot}0 \times 10^5$ dynes, $H\text{–}C\begin{smallmatrix} \diagup \\ O \end{smallmatrix} = H\text{–}C\begin{smallmatrix} \diagup\!\!\diagup \\ O \end{smallmatrix}$ deformation $= 0{\cdot}5 \times 10^5$ dynes $\gamma_{c-h}/\gamma_{c-o} = 0{\cdot}94$, the frequencies calculated are 1738, 1345, 1104 and 319 which are very near the observed values.

Acetic Acid.—Like formic acid, this acid shows weak lines 1720, 882 and 600 accompanying the strong lines 1669, 895 and 620. As in the former, the carbonyl frequency 1720 is depolarised and 1669 is polarised indicating the co-existence of monomer and polymer. Considering (CH_3) group as a single unit of mass 15, the author has solved the secular equation with the probable force-constants, k (C–C) $= 4{\cdot}5$, k_1 (C = O) $= 10$, k_2 (C–O) $= 5{\cdot}0$ $k_3 = k_4\left(C\text{–}C\begin{smallmatrix} \diagup \\ O \end{smallmatrix}\right)$ deformation $= 0{\cdot}4 \times 10^5$ dynes, and $\gamma_{c-o} = \gamma_{c-o} = 1{\cdot}3$ Å, and $\gamma_{c-c} = 1{\cdot}55$ Å, $C\text{–}C\begin{smallmatrix} O \\ \diagup\!\!\diagup \end{smallmatrix} = C\text{–}C\begin{smallmatrix} \diagup \\ O \end{smallmatrix} = 120°$ and has obtained the frequencies 1704, 1280, 833, 413 and 260. It appears correct to assume that the observed frequencies 1720, 1363, 882, and 450 are the planar frequencies of the molecule and 600 is due to a vibration perpendicular to the plane, and that the force constants in the monomer molecule are near those given above. These considerations suggest that acetic acid also possesses a small percentage of the monomer. Of the frequencies mentioned above, 1363, represents the symmetrical oscillation of the carboxyl group, 882 is the C–C frequency and 415 is the $C\text{–}C\begin{smallmatrix} \diagup \\ O \end{smallmatrix}$ deformation frequency.

Hydroxyl frequency in fatty acids.—Both formic and acetic acids show the hydroxyl frequency in the same region, namely, 2932–3466, and the shift from the normal frequency in KOH (3608) is the same in both. Both these acids have the dissociation constants of the same order and the degree of association (Ramsay and Shield's value) is the same for both. It appears likely, as suggested by Venkateswaran (1938) that the shift of the hydroxyl frequency is dependent on the activity of the ionisable hydrogen, the shift being greater the more active the hydrogen is. This is supported by observations on trichloracetic acid where the dissociation constant is two thousand times as high as in acetic acid ($20{,}000 \times 10^{-5}$) and the shift of the hydroxyl frequency is 612.

In conclusion, the author thanks Prof. Sir C. V. Raman for his kind interest in the work.

Summary

The Raman spectra of formic, acetic, dichloracetic and trichloracetic acids have been obtained with a filter of iodine in CCl_4 in order to record the O–H frequencies. Trichloracetic acid has also been studied in different states of aggregation. The changes in the Raman spectra for various states are indicated by the change in the intensities of lines 433, 450, 676 and 833; 450 is present in the solid only, and 433 in solution only while both are present in the liquid. The frequency 676 is sharp and strong in the solid, but weaker and more diffuse as we pass from the solid to solution. The frequencies 1434, 676, 455 and 102 which vanish or become very weak on dilution represent the undissociated molecule, the frequencies 1330, 833, 952, 433 which are strengthened on dilution represent the monomer, the frequencies 202, 284 and 952 which remain unaffected represent both the ion and the undissociated molecule while the frequencies 695, 734, 1750 which appear on great dilutions represent the ionic frequencies. O–H bands have been recorded for all the acids; in the case of trichloracetic acid the band shows a triplet structure the centre of the band being at 2996. The shift of the hydroxyl frequency from the normal value of 3608 is greater in trichloracetic than in formic or acetic acid which is in accordance with Venkateswaran's hypothesis.

The spectra of formic and acetic acids are analysed for the monomer and polymer molecule, and the force constants for the various linkages are suggested.

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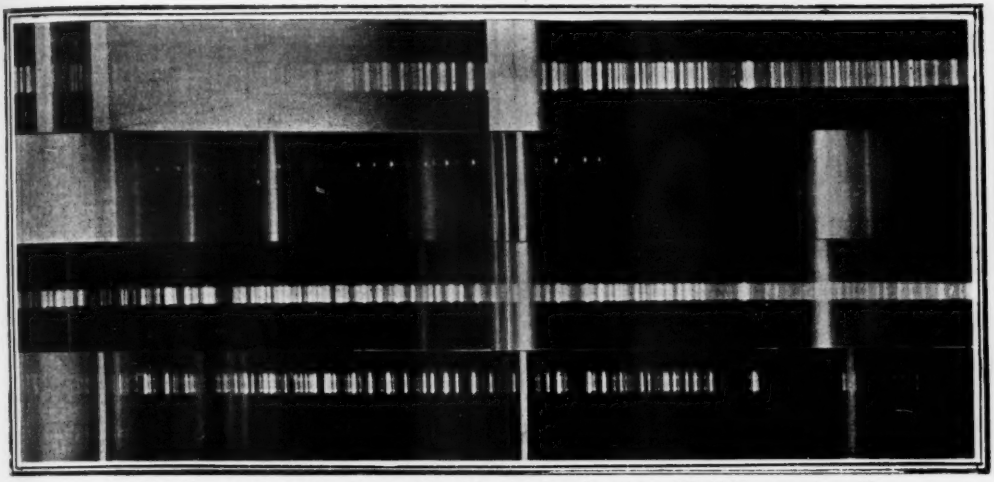
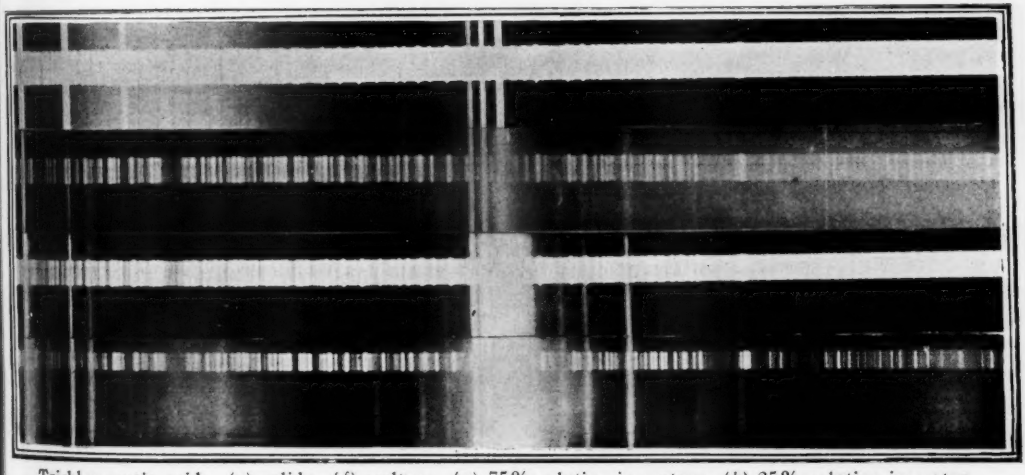
Bonner and Hofstadter	..	*J. Chem. Phy.*, 1938, **6**, 532.

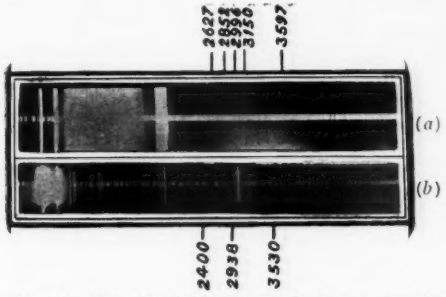
RAMAN SPECTRA



(*a*) Trichlor-acetic acid; (*b*) acetic acid; (*c*) formic acid; (*d*) dichlor-acetic acid



Trichlor-acetic acid; (*e*) solid; (*f*) molten; (*g*) 75% solution in water; (*h*) 25% solution in water



(*a*) Trichlor-acetic acid and (*b*) dichlor-acetic acid showing faint O–H bands

THE RAMAN SPECTRA AND THE MOLECULAR STRUCTURE OF SOME ALIPHATIC CYCLIC COMPOUNDS

(Cyclohexane, Cyclohexanol, Cyclohexanone, Dioxane and Paraldehyde)

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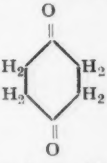
1. *Introduction*

IT is well known from the dipole moment and the electron diffraction studies that the cyclohexane ring is puckered and possesses a *trans* symmetry. This is not always true in the case of the derivatives and the substituted compounds. The compound 1–4 cyclohexane-di-one  shows a dipole moment of 1·6 D (Hassel, 1934) which it would not have if it were completely *trans* ; and in dioxane, which is a ring substituted compound, the dipole moment and the electron diffraction evidence is conflicting. In the present paper, the ring frequencies for the *trans* model (symmetry S_{6u}) of cyclohexane have been worked out and the polarisation and the Raman effect data of different compounds have been analysed in relation to their molecular structures.

2. *Results*

The results of the investigation are listed in Tables I–VIII given in the body of the paper. The polarisation studies for all the compounds excepting cyclohexane have been made for the first time. In cyclohexane the polarisation results were available for the intense lines only, the study now includes the faint lines as well. Using a Littrow glass spectrograph having a dispersion of 6 A.U. in 4046 region and 11 A.U. in the 4358 region, the author has observed the following new lines 1366, 1207, 1168, 980 and 934 in cyclohexanol and 106, 384, and 1184 in cyclohexanone. The frequency measurements of the author are in good agreement with the previous workers,

reference to whose work may be found in the bibliography on the Raman effect by Hibben (1939).

3. *Discussion*

1. *Calculation of the ring frequencies for cyclohexane** :

The model assumed (Wierl, 1931, and Pauling and Brockway, 1937) for the cyclohexane ring is that of a puckered hexagon made of two equilateral triangles (1, 3, 5) and (2, 4, 6) lying in parallel planes one turned through 60° with respect to the other. The atoms lie at the vertices of the triangles and are marked 1, 2, 3, 4, 5, 6 (see Fig. 1). The angle between two valence bonds is taken as 110° and the length of each bond is taken as 1·54 A° from the electron diffraction studies of Pauling and Brockway (1937). The vertices of the two triangles lie on a sphere, and so the centre of gravity of the system is the centre of the sphere. The X-axis passes through the centre of gravity of the system and is parallel to the line (1, 4), Y-axis is perpendicular to this in a plane parallel to the triangular plane, and the Z-axis is perpendicular to the plane of the two triangles. $2a$ is the side of the triangle and $2c$ the distance between the two planes.

(*a*) *The Character table and the symmetry co-ordinates.*—For the proposed structure the symmetry of the molecule is S_{6u}, the elements of symmetry being E, $2S'_6$ (a double six-fold axis of rotation and reflection), $2C_3$ (a double three-fold axis of rotation by $\frac{4\pi}{6}$), i (the centre of symmetry), $3C_2$ (three two-fold axes of rotation by π) and 3 σ_v (three planes of symmetry). These are :

$2\,S_6 \rightarrow$ (1, 2, 3, 4, 5, 6)
(1, 6, 5, 4, 3, 2)

$2\,C_3 \rightarrow$ (1, 3, 5), (2, 4, 6)
(1, 5, 3), (2, 6, 4)

* Since this paper was sent up for publication, a paper by Langseth and Bak has appeared (*Jour. Chem. Phys.*, 1940, **8**, 403) in which the Raman spectra of cyclohexane, cyclohexane-d_1 and cyclohexane d_{12} have been reported and results discussed in relation to their molecular structure. These authors have considered D_{6h}, D_{3d}, C_{2v} and C_2 as possible symmetries for the cyclohexane molecule. The lower symmetries D_2, C_{2v} and C_s are ruled out from considerations of the number of observed Raman lines. Of the other two possible symmetries, D_{3d} should have four totally symmetric frequencies below 1500 which are polarised whereas D_{6h} should have only two symmetric fundamentals in this region. These authors have estimated the state of polarisation of the lines from their shape and observed that in C_6H_{12} only two lines namely 800 and 1158 below 1500 are polarised. This fact has been put forward as supporting D_{6h} symmetry for the molecule. In the present investigation the line 382, which is taken as depolarised by Langseth and Bak is observed as polarised. This can be very clearly seen from the accompanying plate. Besides, the weak line 1348 is also polarised. Thus altogether there are four polarised lines in the region below 1500, which is in agreement with the supposition that the cyclohexane molecule has a *trans* configuration as assumed in this paper.

$i \rightarrow (1, 4), (2, 5), (3, 6)$

$3\,C_2 \rightarrow (1, 2), (3, 6), (4, 5)$
$(2, 3), (1, 4), (5, 6)$
$(3, 4), (2, 5), (1, 6)$

$3\,\sigma_v \rightarrow (1), (4), (2, 6), (3, 5)$
$(2), (5), (1, 3), (4, 6)$
$(3), (6), (2, 4), (1, 5).$

The character table, the number of modes of vibration, and the selection rules for the Raman and infra red frequencies are given in the following table :

TABLE I

$S_{6\nu}$	E	$2S'_6$	$2C_3$	i	$3\sigma_v$	$3C_2$	No. of ring vibrations			Selection rules		No. of vibrations for the molecule	
							Total	Internal	Translation and Rotation	Raman	Infra-red	Total	Internal
A_1	1	1	1	1	1	1	2	2	0	*pol*	*ia*	6	6
A_2	1	1	1	1	−1	−1	1	0	1 T	*v*	*ia*	3	2
B_1	1	−1	1	−1	1	−1	2	1	1 R	*v*	*a*	6	5
B_2	1	−1	1	−1	−1	1	1	1	0	*v*	*ia*	3	3
E_1	2	1	−1	−2	0	0	3	2	1 T	*v*	*a*	9	8
E_2	2	−1	−1	2	0	0	3	2	1 R	*dep.*	*ia*	9	8
U_R	6	0	0	0	2	0							
ϵ_R	12	0	0	0	6	6							

v–forbidden ; *ia*–inactive ; *a*–active.

Symmetry co-ordinates for ring frequencies.—For determining the potential and kinetic energies of a molecule, the co-ordinates of every atom are to be referred with respect to its equilibrium position as origin. x_k, y_k, z_k are the co-ordinates of the kth atom, x_k points to the centre of the triangle in which it lies, y_k is at right angles to this direction being positive in the right handed sense; and z_k is perpendicular to both these, being positive in the upward direction for atoms (1, 3, 5) and positive in the downward direction for atoms (2, 4, 6). The following normal co-ordinates are obtained :

A_1 $\quad x_1+x_2+x_3+x_4+x_5+x_6$ $\quad Q'_1$

$\quad z_1+z_2+z_3+z_4+z_5+z_6$ $\quad Q'_z$

A_2 $\quad y_1+y_2+y_3+y_4+y_5+y_6$ $\quad Q_{wz}$

B_1 $\quad z_1+z_3+z_5-z_2-z_4-z_6$ $\quad Q'_2$

$\quad x_1+x_3+x_5-x_2-x_4-x_6$ $\quad Q_3$

B_2 $\quad y_1+y_3+y_5-y_2-y_4-y_6$ $\quad Q_4$

E_1 $\quad 2(x_1-x_4)+(x_2-x_5)-(x_3-x_6)+\sqrt{3}(y_2-y_5)+\sqrt{3}(y_3-y_6)$ $\quad Q_x$

$\quad 2(y_1-y_4)+(y_2-y_5)-(y_3-y_6)-\sqrt{3}(x_2-x_5)-\sqrt{3}(x_3-x_6)$ $\quad Q_y$

E_1 (ii) $\quad 2(x_1-x_4)+(x_2-x_5)-(x_3-x_6)-\sqrt{3}(y_2-y_5)-\sqrt{3}(y_3-y_6)$ $\quad Q'_{5a}$

$\quad 2(y_1-y_4)+(y_2-y_5)-(y_3-y_6)+\sqrt{3}(x_2-x_5)+\sqrt{3}(x_3-x_6)$ $\quad Q'_{5b}$

E_1 (iii) $\quad 2(z_1-z_4)+(z_2-z_5)-(z_3-z_6)$ $\quad Q'_{6a}$

$\quad \sqrt{3}(z_2-z_5)+\sqrt{3}(z_3-z_6)$ $\quad Q'_{6b}$

E_2(i) $\quad \left[\frac{c}{2}\left\{2(x_1+x_4)-(x_2+x_5)-(x_3+x_6)-\sqrt{3}(y_2+y_5)+\sqrt{3}(y_3+y_6)\right\}+\frac{a}{\sqrt{3}}\left\{2(z_1+z_4)-(z_2+z_5)-(z_3+z_6)\right\}\right]$ $\quad Q_{wy}$

$\quad \left[\frac{c}{2}\left\{\sqrt{3}(x_2+x_5)-\sqrt{3}(x_3+x_6)+2(y_1+y_4)-(y_2+y_5)-(y_3+y_6)\right\}+\frac{a}{\sqrt{3}}\left\{\sqrt{3}(z_2+z_5)-\sqrt{3}(z_3+z_6)\right\}\right]$ $\quad Q_{wx}$

E_2 (ii) $\quad \left[\frac{a}{\sqrt{3}}\left\{2(x_1+x_4)-(x_2+x_5)-(x_3+x_6)-\sqrt{3}(y_2+y_5)+\sqrt{3}(y_3+y_6)\right\}+c\left\{-2(z_1+z_4)+(z_2+z_5)+(z_3+z_6)\right\}\right]$ $\quad Q'_{7a}$

$\quad \left[\frac{a}{\sqrt{3}}\left\{2(y_1+y_4)-(y_2+y_5)-(y_3+y_6)+\sqrt{3}(x_2+x_5)-\sqrt{3}(x_3+x_6)\right\}+c\left\{-\sqrt{3}(z_2+z_5)+\sqrt{3}(z_3+z_6)\right\}\right]$ $\quad Q'_{7b}$

E_2 (iii) $\quad 2(x_1+x_4)-(x_2+x_5)-(x_3+x_6)+\sqrt{3}(y_2+y_5)-\sqrt{3}(y_3+y_6)$ $\quad Q'_{8a}$

$\quad \sqrt{3}(x_2+x_5)-\sqrt{3}(x_3+x_6)-2(y_1+y_4)+(y_2+y_5)+(y_3+y_6)$ $\quad Q'_{8b}$

These are diagrammatically represented in Fig. 1.

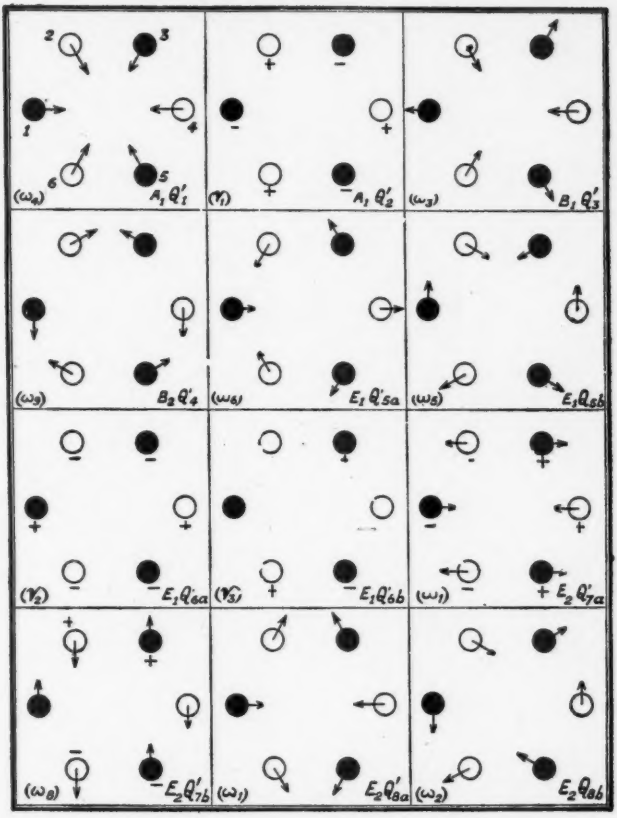


FIG. 1

(*b*) *Calculation of ring frequencies* :

The potential energy of the system due to the vibration is given by $2V = \Sigma k_1 (\Delta R)^2 + \Sigma d (\Delta \phi)^2$ where k_1 is the valence force constant for the C–C bond and d the force constant for angular deformation C⟨C⟩C $\left(d' = \frac{d}{R^2 \sin^2 \phi}\right)$, R is the bond distance between two successive atoms and ϕ is the angle between two successive bonds at any atom, ΔR and $\Delta \phi$ denote the variations of R and ϕ. The method of calculating the frequencies has been indicated by the author in an earlier paper (Saksena, 1939).

The frequencies λ_1 and λ_2 are the roots of the quadratic

$$\left[\frac{4}{3}\frac{a^2}{R^2}k_1+\frac{a^2}{R^2}d'\left\{12+\frac{16}{3}(1-\cos\phi)^2+16(1-\cos\phi)\right\}-m\lambda^2\right]\times$$
$$\left[16\frac{c^2}{R^2}k_1+64\frac{c^2}{R^2}d'(1-\cos\phi)^2-m\lambda^2\right]-$$
$$\left[\frac{8}{3}\frac{ac}{R^2}k_1-\frac{d'}{R^2}ac\left\{16\sqrt{3}(1-\cos\phi)-\frac{32}{\sqrt{3}}(1-\cos\phi)^2\right]^2=0 \quad (1)\right.$$

$$\lambda_3^2=12\frac{a^2}{R^2}\frac{d'}{m} \quad (2)$$

$$\lambda_4^2=4\frac{a^2}{R^2}\frac{k_1}{m} \quad (3)$$

$$\lambda_5^2+\lambda_6^2=2\left\{\frac{a^2+c^2}{R^2}\frac{k_1}{m}+\frac{3d'}{m}\left(\frac{a^2\cos^2\phi+6c^2(1-\cos\phi)^2}{R^2}\right)\right. \quad (4)$$

$$\lambda_5^2\lambda_6^2=72k_1d'a^2c^2/m^2R^4 \quad (5)$$

λ_7 and λ_8 are the roots of

$$\left[\frac{2}{3}\frac{a^2}{R^2}k_1+\frac{2d'}{R^2}a^2\left\{3+\frac{(1-\cos\phi)^2}{3}-2(1-\cos\phi)\right\}-m\lambda^2\right]\times$$
$$\left[\frac{2k_1}{R^2}\left(\frac{4a^2}{3}+2c^2\right)^2+\frac{2d'}{R^2}(1-\cos\phi)^2\left(\frac{4a^2}{3}+2c^2\right)^2-m\left(\frac{4a^2}{3}+2c^2\right)\lambda^2\right]$$
$$-\frac{a^2}{3}\left[\frac{2k_1}{R^2}\left(\frac{4a^2}{3}+2c^2\right)-\frac{2d'}{R^2}(1-\cos\phi)\left(\frac{4a^2}{3}+2c^2\right)(2+\cos\phi)\right]^2=0 \quad (6)$$

If $c=0$ and $\phi=120°$, the points 1, 3, 5 and 2, 4, 6 come in the same plane and we get the benzene structure. The above formulæ now give the frequencies of the benzene ring, and we find

$$\left(\text{using } \frac{a^2}{R^2}=\frac{3}{4},\ \cos\phi=-\frac{1}{2},\ d_1=\frac{d}{R^2}\right)$$

$$\lambda_1^2=\frac{k_1}{m},\ \lambda_2^2=0,\ \lambda_3^2=\frac{12d_1}{m},\ \lambda_4^2=\frac{3k_1}{m},\ \lambda_5^2=\frac{3}{2}\left(\frac{R_1+d_1}{m}\right),$$

$\lambda_6^2=0$, and the expression for λ_7 and λ_8 becomes

$$\left(\frac{k_1+3d_1}{2}-m\lambda^2\right)(2k_1+6d_1-m\lambda^2)-(k_1-3d_1)^2=0$$

so that $\lambda_7^2+\lambda_8^2=\frac{5}{2}\frac{k_1+3d_1}{m}$, $\lambda_7^2\lambda_8^2=\frac{12k_1d_1}{m}$.

These expressions may be compared with those obtained by Bossche and Manneback (1934) for the benzene ring and also with those recorded on page 73 of 'Der Smekal-Raman Effekt, Erganzungsband, by Kohlrausch. The terms $n_{1,2}$, n_3, n_4, $n_{5,6}$, $n_{7,8}$, n_9 of Kohlrausch represent λ_5, λ_3, λ_1, λ_7, λ_8, and λ_4 respectively in our case. The zero value of λ_2 and λ_6 indicates that these frequencies are no longer in the same class as λ_1 and λ_5 respectively and also that there are no variations of bond lengths and bond angles in these oscillations.

2. *Analysis of the Raman Spectrum of Cyclohexane*

The observed Raman frequencies, their states of polarisation ρ, the infra-red spectrum as observed by Le Comte and Lambert (1932) and Le Comte (1938) are given in Table II. Rousset's (1933) values for ρ are given for comparison.

TABLE II

Raman Frequencies for Cyclohexane C_6H_{12}

Raman Frequency in cms.$^{-1}$	ρ		Infra-red Frequency
	Author	Rousset	
382 (1)	0·47	..	..
426 (3)	0·70	..	..
600 (½)	D	..	525 (m) 678 (*m*)
..	..	..	719 (F)
802 (12)	0·06	0·06	793 (*f*)
..	..	..	865 (F)
..	..	..	906 (F)
1029 (8)	0·78	0·70	1028 (F)
1156 (4)	0·53	..	..
1265 (10)	0·78	0·70	1270 (*f*)
1348 (2)	P	P	1324 (*ss*)
1442 (6)	0·84	D	1436 (*st*)
2467 (0)	P	..	..
2605 (0)	P	..	..
2630 (1)	P	..	..
2662 (2)	P	..	..
2695 (1)	?	..	..
2853 (10)	0·11	0·10	2780 (*st*) 2860
2883 (3)	?	D	..
2922 (6)	P?	D	..
2937 (6)	P	P	2940

According to Kohlrausch and co-workers (1936) the weak lines at 2351 and 2467 are spurious and the lines from 2605 to 2695 do not represent

fundamental frequencies. However, Ananthakrishnan (1936) has observed in addition to these lines, two more lines at 2870 and 2898; but these could not be resolved by the spectrograph used by the author. The line 2922 has a higher degree of depolarisation than its companion 2937 but is not depolarised as reported by Rousset.

Among the six polarised lines belonging to class A_1, two belong to the ring. The latter may be identified with the lines 382 and 802 and the remaining four with the lines 1156, 1348, 2853 and 2937 which are the deformation and the valence (C–H) frequencies. Among the eight degenerate lines belonging to the Raman active class E_2, two belong to the ring. There are three depolarised lines in the region below 1400 cms.$^{-1}$ namely, 426, 1029 and 1265. One of the ring frequencies is naturally the low frequency line 426, and for the other, one has to choose between the two remaining frequencies. But both the lines 1029 and 1265 are intense and depolarised, and appear strongly in the spectra of the derivatives. Kohlrausch (1936) has selected the latter basing his calculations of cyclohexane frequencies on the Bossche-Manneback formulæ for calculating the frequencies of the benzene ring. This is not correct. We calculate below the ring frequencies of the cyclohexane molecule from the formulæ derived before. The force constants k_1 and d' are first calculated from the formulæ for class A_1 by assuming the two frequencies 802 and 382 for this class. This gives $k_1^{(c-c)} = 3{\cdot}77 \times 10^5$ dynes and d' C$\diagup\!\!\overset{C}{\diagdown}$C $= {\cdot}503 \times 10^5$ dynes. With these force constants other frequencies are calculated and given in Table III.

TABLE III

Class	Calculated Frequencies	Observed Frequencies		Notation Adopted
		Raman Effect	Infra-red	
A_1	(802)*	(802)	*f*	ω_4
	(382)*	(382)	*f*	γ_1
B_1	704	*f*	719 (*st*)	ω_3
B_2	1110	*f*	*f*	ω_9
E_1	208	*f*	( )	γ_{23}
	924	*f*	906 (*st*)	$\omega_{5,6}$
E_2	1086	1028	*f*	$\omega_{7,8}$
	427	426	*f*	$\omega_{1,2}$

* Adopted for calculating force Constants.

According to our calculations, the ring frequencies coming in the degenerate class E_2 are 1028 and 426. The infra-red frequency corresponding to the calculated frequency 208 is not known but in many derivatives like piperidine, penta-methylene oxide, morpholin, thioxane etc.,—in which the absence of symmetry makes the vibration $\gamma_{2,3}$ Raman active—a weak Raman line has been observed in the neighbourhood of 200 cms.$^{-1}$ The presence of only two polarised and two depolarised ring frequencies in Raman Effect is strongly in favour of the *trans*-symmetry for the ring. In the *cis* form the molecule should have four polarised and eight depolarised ring frequencies, the symmetry of the form being (C_{2v}). γ_2. ω_1, ω_4, and ω_7 are polarised, and γ_1 is depolarised in this case. If the *cis* form is present, its presence will be revealed by a close depolarised companion to the line 384, but in spite of long exposures neither any faint line nor a differential polarisation in different parts of this line was observed.

3. *Cyclohexanol and Cyclohexanone*

The Raman frequencies and the state of polarisation of Raman lines are given in Tables IV and V. Both these compounds differ from cyclohexane in that one of the H_2 groups is replaced by a HOH group in the first and by an oxygen atom in the second with the result that the symmetry of the cyclo-

TABLE IV

Raman Frequencies of Cyclohexanol

Raman Frequencies	ρ	Raman Frequencies	ρ
2937 (8)	0·56	1130 (1)	P
2927 (2)	P	1070 (1)	P
2859 (8)	0·23	1048 (2)	D
2678 (1)	P	1026 (4)	0·78
1443 (6)	0·83	980 (0)	D
1366 (1)	D	934 (1)	P
1355 (2)	D	840 (3)	0·47
1302 (0)	..	790 (6)	0·27
1260 (3)	0·78	556 (3)	0·47
		477 (1)	P
1207 (1)	P	453 (1)	D
1168 (0)	..	408 (1)	D
		345 (6)	..

TABLE V

Raman Frequencies of Cyclohexanone

Raman Frequencies	ρ	Raman Frequencies	ρ
2950 (4)	0·59	1019 (3)	0·86
2902 (1)	0·40	996 (1)	D
2862 (4)	0·27	912 (1) *br*	0·69
1707 (4)	0·67	840 (4)	0·41
1449 (4)	0·86	790 (0)	P
1422 (2)	0·83	750 (8)	0·30
1346 (1)	D	653 (4)	0·43
1314 (2)	0·71	485 (1)	P
1262 (1)	P	409 (2)	0·78
1246 (1)	D	348 (0)	P
1221 (1)	D	314 (0)	P
1184 (0)	P		
1113 (3)	0·44	150 (0)	?
1076 (1)	D	106 (2)	D

hexane molecule does not exist in them. The molecule of cyclohexanol has only one plane of symmetry (Point group C_s). Hence the molecule should have 29 polarised and 22 depolarised lines and the ring seven (γ_1, γ_2, ω_1, ω_3, ω_4, ω_6, ω_7) polarised and five (γ_3, ω_2, ω_5, ω_8, ω_9) depolarised. Seven polarised and three depolarised lines are observed in the region 0–1400 showing that the molecule has a puckered structure.

Assuming that the oxygen atom in cyclohexanone lies in the plane of the neighbouring carbon bonds, the molecule will have a symmetry C_{2v} if the ring is plane, and will belong to the symmetry class C_s if it is puckered. The number of polarised and depolarised lines for both these classes are :

Symmetry Class	Number of Raman lines for the molecule		Number of Raman lines for the ring	
	Polarised	Depolarised	Polarised	Depolarised
C_{2v} ..	14	31	6	9
C_s ..	25	20	9	6

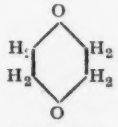
In the region below 1200 *i.e.*, in the region of the ring nine polarised and six depolarised lines are observed. This fact indicates a puckered structure for the ring.

The number of lines observed in these compounds is much less than the expected number, perhaps the other lines are too weak to be observed.

The following are probably the ring frequencies :

	γ_1	γ_2	γ_3	ω_1	ω_2	ω_3	ω_4	ω_6	ω_5	ω_7	ω_8
Cyclohexanol ..	406	..	.	477	453	840	790	934	980	1025	1070
Cyclohexanone ..	348	..	..	485	409	840	750	912	996	1020	..

4. *Dioxane* :—

The molecule of dioxane has a structure  containing a cyclo-

hexane ring in which the opposite carbon atoms are replaced by oxygen atoms. As in cyclohexane, the ring in dioxane is puckered. The Raman and the infra-red measurements are in favour of ascribing a predominantly *trans* form for the molecule. The present investigation, however, shows that a definite fraction of the substance exists in the *cis* form in the liquid state.

The four probable forms (Fig. 2) of the molecule of dioxane are (1) the plane with a symmetry D_{2h} (2) the puckered *trans* with a symmetry C_{2h} (3)

Trans Cis (symmetrical Cis (unsymmetrical)

FIG. 2

● Carbon atoms. ○ Oxygen atoms.

the puckered *cis* with a symmetry C_{2v} and (4) the puckered unsymmetrical *cis* form considered by Kubo (1936) in which there is one symmetry axis C_2 perpendicular to the plane of four C and O atoms. The former three forms have been considered by Kohlrausch and Stockmair (1936). In Table VI, the number of Raman active lines for the different forms are stated along with their polarisation characters.

TABLE VI

Form of the molecule	Symmetry Class	Raman lines for the molecule		Raman lines for the ring	
		Pol.	Dep.	Pol.	Dep.
Plane ..	D_{2h}	6	12	3	3
Trans ..	C_{2h}	10	8	4	2
Cis ..	C_{2v}	10	26	4	8
Asymmetric cis	C_2	19	17	7	5

The results obtained by the author for the depolarisation ratios of the Raman lines of dioxane, observed by Venkateswaran (1935) are given in Table VII together with the infra-red frequencies recently measured by McKinney and Warner (1937) and Le Comte (1938).

TABLE VII

The Raman Frequencies of Dioxane

Raman Frequency	ρ	Infra-red Frequency	Raman Frequency	ρ	Infra-red Frequency
3064 (1)	P	3118	1222 (5)	·75	1256
2966 (10)	·57	2961 (*v. s.*)	1209 (1)	D	
2890 (2)	·60	2891 (*v. s.*)	1124 (3)	·65	1122 (*v. s.*)
2853 (8)	·33	2885 (*v. s.*)	1109 (3)	·76	1083 (*s*)
					1048 (*s*)
2785 (3)	·53	2752 (*m*)	1012 (6)	·75	1017 (*s*)
2719 (1)	·53	2690 (*m*)	946 (1)	D	887 (*v. s.*)
2661 (0)	P				874, 870
1451 (2)	D	1452 (*s*)	849 (1)	D	
1444 (8)	·76		836 (8)	·37	
1328 (2)	P	1323 (*s*)	482 (4) 433 (2)	·82 ·61	
1306 (8)	·73	1289 (*v. s.*)	426 (0) 243 (1)	P D	

The spectrum shows ten polarised and twelve depolarised lines. The author does not find any justification for excluding the lines 243, 426, 946, 1209 and 2773 reported by Venkateswaran, as has been done by Kohlrausch and Kahovec (1937). The polarisation results exclude the plane and the asymmetric *cis* form. The observed number of ten polarised lines agrees with both the *cis* and *trans* forms but the number of depolarised lines observed is definitely greater than that required for the *trans* form. The results suggest that while dioxane exists for the most part in the *trans* form a small percentage of the *cis* form is also present. The intense Raman lines corresponding to the latter will therefore appear weakly. The dioxane spectrum shows that the strong Raman lines 836, 1222, 1306 and 1444 are accompanied by faint companions at 849, 1209, 1328 and 1451 respectively. The infra-red spectrum also shows several coincidences with the Raman spectrum all of which may not be accidental, although there is no infra-red absorption corresponding to the intense Raman line 836. Such coincidences are not allowed for the *trans* form but are possible for the *cis* form.

In the region 0–1400 altogether five polarised and 8 depolarised lines are observed. Of these, four polarised lines at 420, 433, 836 and 1124 and two depolarised lines at 482 and 1109 can be assigned to the ring frequencies γ_1, ω_1, ω_4 and ω_7 (polarised) and ω_2, ω_8 (depolarised) in accordance with the *trans* symmetry of the molecule. The very weak companion lines at 1451, 1328, 1209, 849 and the weak line 243 may be assigned to the *cis* form. This conclusion is also supported by the presence of a small positive dipole moment (0·43–0·490) reported by Smyth and Walls (1931), Williams (1930), Hunter and Partington (1933), and Kubo (1936). Sutton and Brockway (1935), however, report a *trans* structure for the molecule from electron diffraction measurements.

(5) *Paraldehyde* :

Electron diffraction measurements by Ackerman and Meyer (1936) indicate that the ring is a puckered hexagon with the carbon atoms and oxygen atoms in two parallel planes at a distance of 0·47Å. The carbon atoms of the three CH_3 groups lie in another parallel plane at a distance of 0·57Å from the carbon atoms. The symmetry of the molecule is C_{3v}. The vibrations can be grouped into three classes, symmetric, anti-symmetric and degenerate.

C_{3v}	E	$2C_3$	$3\sigma v$	Number of vibrations		Selection rules	
				Molecule	Ring	Raman	Infra-red
A	1	1	1	12	3	*p*	*a*
B	1	1	−1	7	1	*ia*	*ia*
E	2	1	0	19	4	*dep.*	*a*
u_R	21	0	5				
ϵ_R	57	0	15				

The total number of lines recorded is 22 of which eleven are polarised and eleven depolarised. The ring frequencies are

$\gamma_1 = 525$, $\gamma_{2,3} = 275$, $\omega_{1,2} = 470$, $\omega_3 = 945$,
$\omega_4 = 840$, $\omega_{5,6} = 1190$ and $\omega_{7,8} = 1345$,

which correspond to the four totally symmetrical and three degenerate Raman-active frequencies. The polarisation results are given in the accompanying table.

TABLE VIII

Raman Frequencies of Paraldehyde

Raman Frequency	ρ	Infra-red	Raman Frequency	ρ	Infra-red
2998 (4)	·85		1191 (3)	D	
2941 (6)	·13		1173 (3)	·70	
2878 (0)	..	2882 (*s*)	1102 (4)	·66	1093 (*v. s.*)
2849 (2)	·37		956 (1)	P	945 (*v. s.*)
2779 (1)	·43		852 (1)	D	855 (*v. s.*)
			839 (6)	·53	
2726 (1)	·62		741 (0)	D	746 (*s*)
2671 (0)	P	2000 (*s*)	574 (1)	D	
		1961 (*w*)			
		1754 (*w*)	524 (10)	·13	
		1613 (*v. s.*)	471 (6)	·85	
1449 (6)	·89	1449 (*s*)	273 (3)	·85	
1369 (5)	·83	1381	178 (1)	·83	

The infra-red spectrum reported by Coblentz is not complete, but the observed frequencies agree reasonably well with the Raman frequencies. These results are thus in agreement with the puckered structure of the molecule.

In conclusion, the author thanks Prof. Sir C. V. Raman for his kind interest in the work.

Summary

The symmetry co-ordinates and the formulæ for the ring frequencies of the cyclohexane molecule (symmetry $S_{6\,u}$—*trans* form) have been obtained by employing the methods of group-theory. These are easily reduced to the formulæ for the benzene ring frequencies given by Bossche and Manneback. Using the frequencies 802 and 382 (both polarised) as belonging to class A_1 the C–C force constant (k_1) is calculated as $3{\cdot}77 \times 10^5$ dynes and d' $\left(C\diagup\!\!\diagdown^{C}\!\!\diagup\!\!\diagdown C\right)$ deformation as $\cdot 503 \times 10^5$ dynes. Other frequencies calculated with these force constants are 709 [obs., 719 (st.) in infra-red] for class B_1, 1110 (forbidden in both Raman effect and infra-red) for B_2, 208 and 924 [obs. 906 (st.) in infra-red] for class E_1 and 427 and 1086 (obs. 426 and 1028 in Raman effect) for class E_2.

The Raman spectra and polarisation measurements have been obtained for cyclohexane, cyclohexanol, cyclohexanone, dioxane, and paraldehyde. The polarisation data for the last four compounds have been obtained for the first time. Several new frequencies at 1366, 1207, 1168, 980 and 934 have been observed in cyclohexanol and at 106, 384 and 1184 in cyclohexanone. Polarisation results show that while cyclohexane exists in a purely *trans* form, dioxane exhibits a predominantly *trans* form with a small fraction of the *cis* form as well. The weak lines at 849, 1209, 1328 and 1451 have been assigned to the *cis* form of dioxane. Paraldehyde, cyclohexanol, and cyclohexanone show puckered structures.

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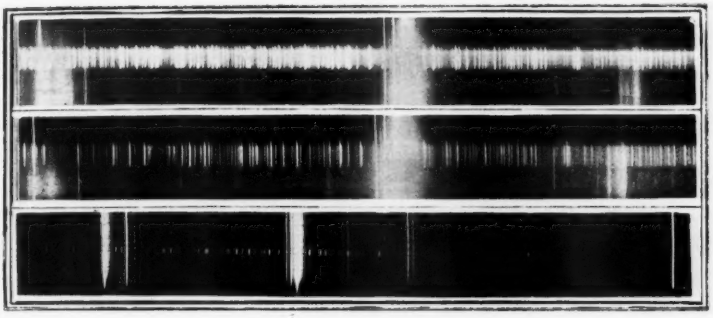
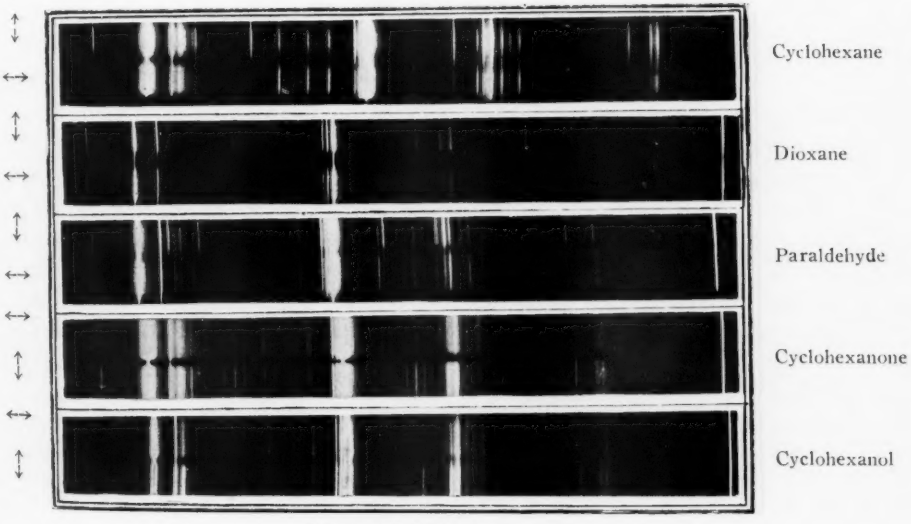
RAMAN SPECTRA





State of Polarisation

MODIFIED REFLECTION OF X-RAYS BY CRYSTALS: CALCITE

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1. *Introduction*

In a note under the title 'A New X-Ray Effect', Raman and Nilakantan[1] have recently described the essential features of a new type of X-Ray reflection which may be looked upon as the analogue in X-ray optics of the now familiar Raman scattering by crystals. In a series of subsequent papers,[2] the results of a detailed study in diamond and sodium nitrate have been described and discussed by these authors.* Raman and Nagendra Nath[3] have also outlined a formal theory of this phenomenon and derived the more important laws which govern the same.

The authors are now engaged in a study of this effect and the detailed measurements which are planned are still in progress. Nevertheless, it is thought desirable to publish here an account of the preliminary results obtained with calcite in view of the novelty of the phenomenon.

2. *Experimental Details and Results*

A plate of calcite with its faces parallel to a cleavage plane (211) has been used in this investigation. The source of X-rays is a Shearer tube with a copper anticathode. The Cu K_α and Cu K_β rays along with a certain amount of white radiation are present in the incident beam. The crystal is so mounted that the incident beam falls on the (211) planes, which have a spacing of 3·029 A.U., at approximately the correct Bragg angle for Cu K_α radiation. A series of five pictures reproduced in Fig. 1 are obtained for angles of incidence which deviate slightly and progressively from this setting. On account of the heavy absorption of X-rays in the fairly thick plate of calcite chosen, the investigation could not be pushed to angles of incidence which differ widely from the correct Bragg angle. Fig. 1*a* refers to the initial setting. In Figs. 1*b*, *c*, *d* and *e*, the angles of incidence are 1°, 2°, 2½° and 3°

* Siegel and Zachariasen (*Phys. Rev.*, 1940, **57**, 795) have reported the appearance of subsidiary diffraction maxima in X-ray scattering which presumably have a similar origin. Their investigations have, however, been confined to the very close neighbourhood of the correct Bragg setting.

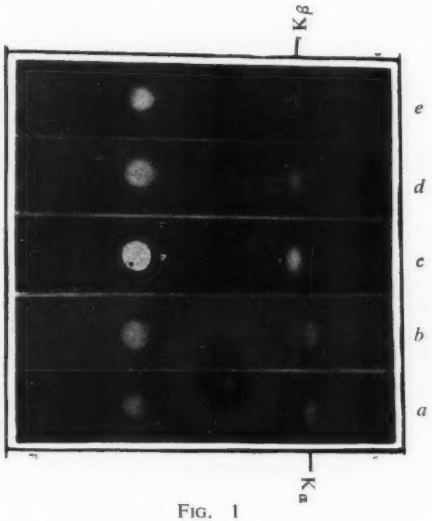

FIG. 1

Showing modified reflections due to Cu K_α and Cu K_β radiations from (211) planes of calcite

respectively less than the initial setting. The modified spots due to K_α are clearly seen in Figs. 1*a*, *b* and *c* and those due to K_β are clearly seen in Figs. 1*b*, *c*, *d* and *e* while the Laue spot due to the (211) planes, which apparently falls on the top of the K_α modified spot in Fig. 1*b* and on the top of the K_β modified spot in Fig. 1*c*, may be seen clearly separated in Figs. 1*d* and *e*. Results of measurement and calculation are given below in Table I.

TABLE I

Modified Reflections from (211) *Planes of Calcite*

Setting	Spot distance from centre	$\theta + \phi$	Spacing
Fig. 1 *a* ..	2·67 α	29° 30′	3·018
„ 1 *b* ..	2·67 α	29° 30′	3·018
„ 1 *b* ..	2·38 β	26° 46′	3·002
„ 1 *c* ..	2·66 α	29° 24′	3·029
„ 1 *c* ..	2·40 β	26° 57′	2·983
„ 1 *d* ..	2·40 β	26° 57′	2·983
„ 1 *e* ..	2·38 β	26° 46′	3·002

α and β denote that the spots arise from Cu K_α and Cu K_β respectively. The plate distance employed is 4·72 cms. and $\theta + \phi$ stands for the total deviation produced in the X-ray beam on reflection. The spacing, calculated with the help of the symmetrical formula $2d \sin \frac{1}{2}(\theta + \phi) = \lambda$, is given in column 4 in each case.

3. *Discussion of Results*

The standard value of 3·029 A.U. for the (211) spacing of calcite may be compared with the figures given in column 4 of Table I. Results based on the symmetrical formula alone have been given in this table. Raman and Nilakantan have suggested an unsymmetrical formula also which was found by them to hold good in the case of diamond. Application of this to calcite leads to more or less the same spacing values as are given in column 4 of Table I and is not therefore separately considered here. The range of investigation has, in fact, been so narrow that the experimental results obtained cannot decide in favour of one or other of these alternative formulæ. The rapid fall in the intensity of the Laue spot as well as the modified spots, as we move away from the correct Bragg setting, may be attributed to the relatively small amount of white radiation that is present in the incident beam and the large absorbing power of calcite.

4. *Summary*

Modified X-ray reflections, due to Cu K_α and Cu K_β radiations from the (211) planes of calcite, have been recorded. Their positions are measured and the results lead to a spacing which remains nearly constant for all the settings studied. This agrees well with the standard value, namely 3·029 A.U.

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